HIGH-PRESSURE SYNCHROTRON INFRARED SPECTROSCOPY:

New Light on Materials under Extreme Conditions

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Carnegie Institution

OUTLINE

I. Introduction

STATIC HIGH-PRESSURE SCIENCE

UNIQUE ADVANTAGES OF SYNCHROTRON INFRARED

II. Highlights: A Decade of New Findings

SELECTED APPLICATIONS:

Physics, Chemistry, Materials Science,
Earth and Planetary Science, Biology and Soft Matter

III. New Opportunities and Challenges

SELECTED GRAND CHALLENGES

A NEW OF HIGH-PRESSURE DEVICES

POSSIBLITIES FOR NSLS-II

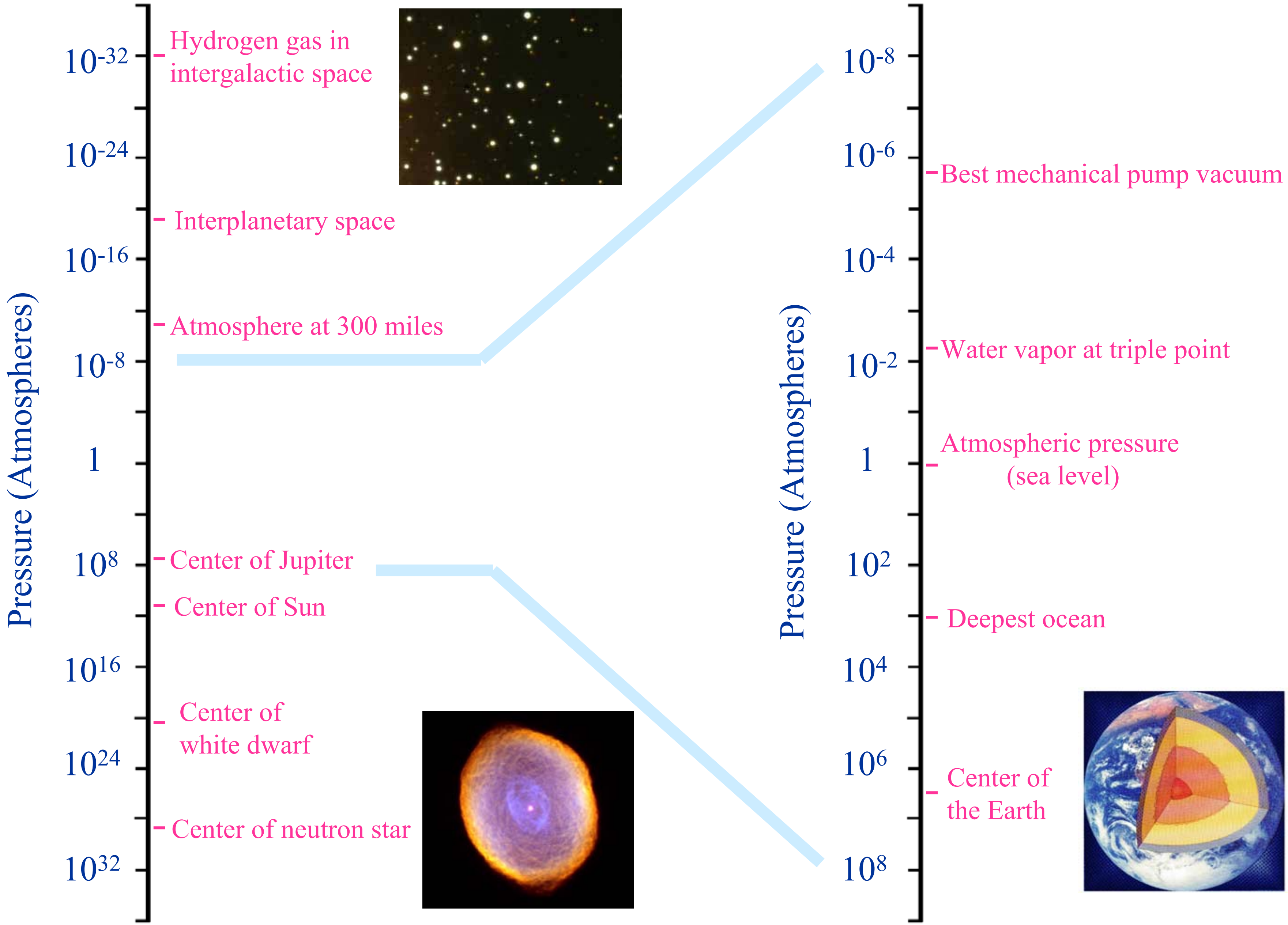
THEMES

Synchrotron infrared and high pressure
- an extraordinary match

Synchrotron IR/x-ray probes
- unique capabilities of the NSLS

Full integration of techniques
- future facilities

RANGE OF PRESSURE IN THE UNIVERSE

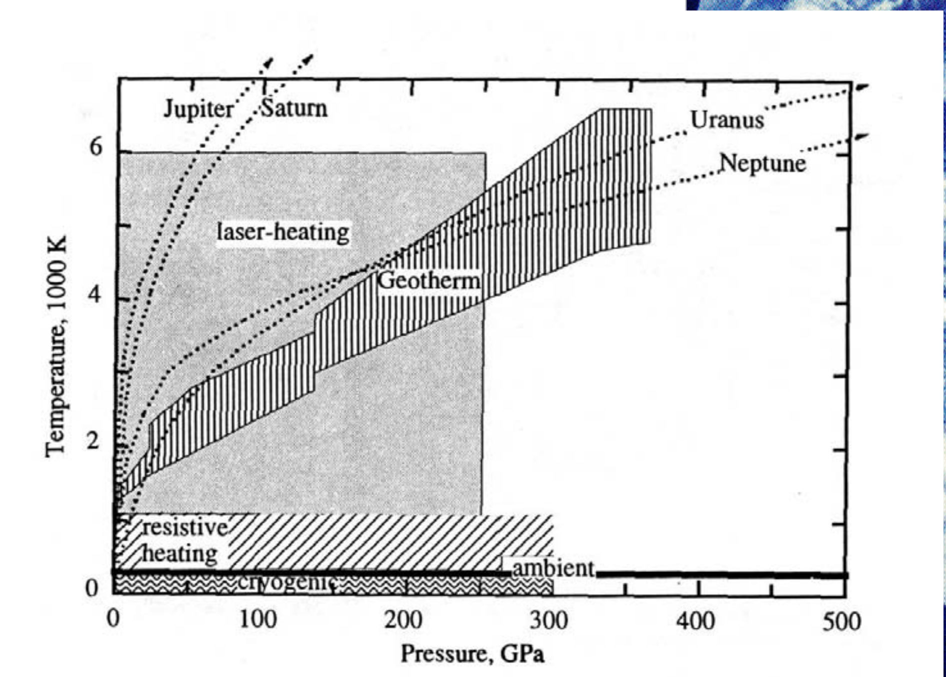


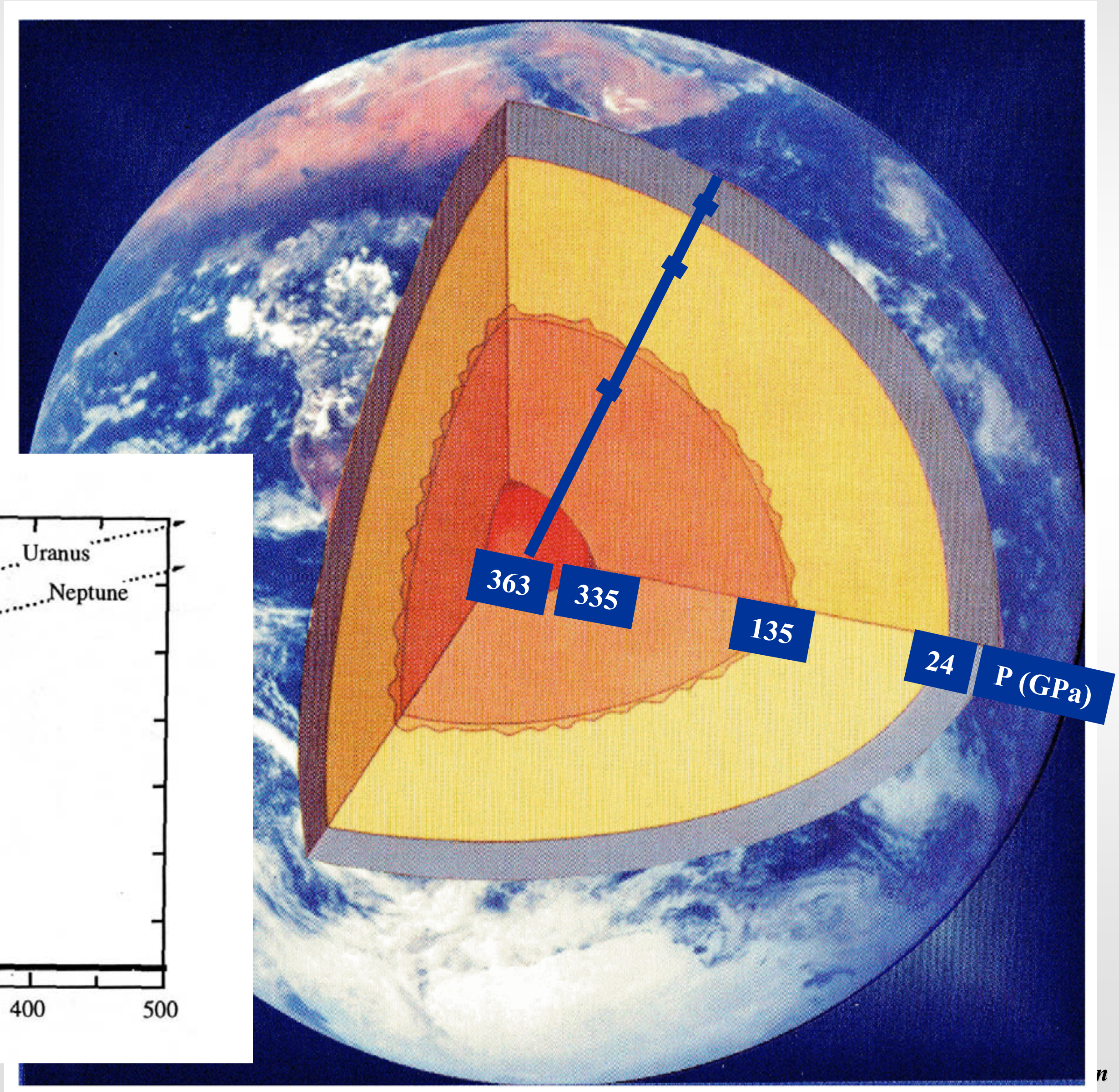
ADVANCES IN STATIC HIGH PRESSURE

PRESSURE UNITS

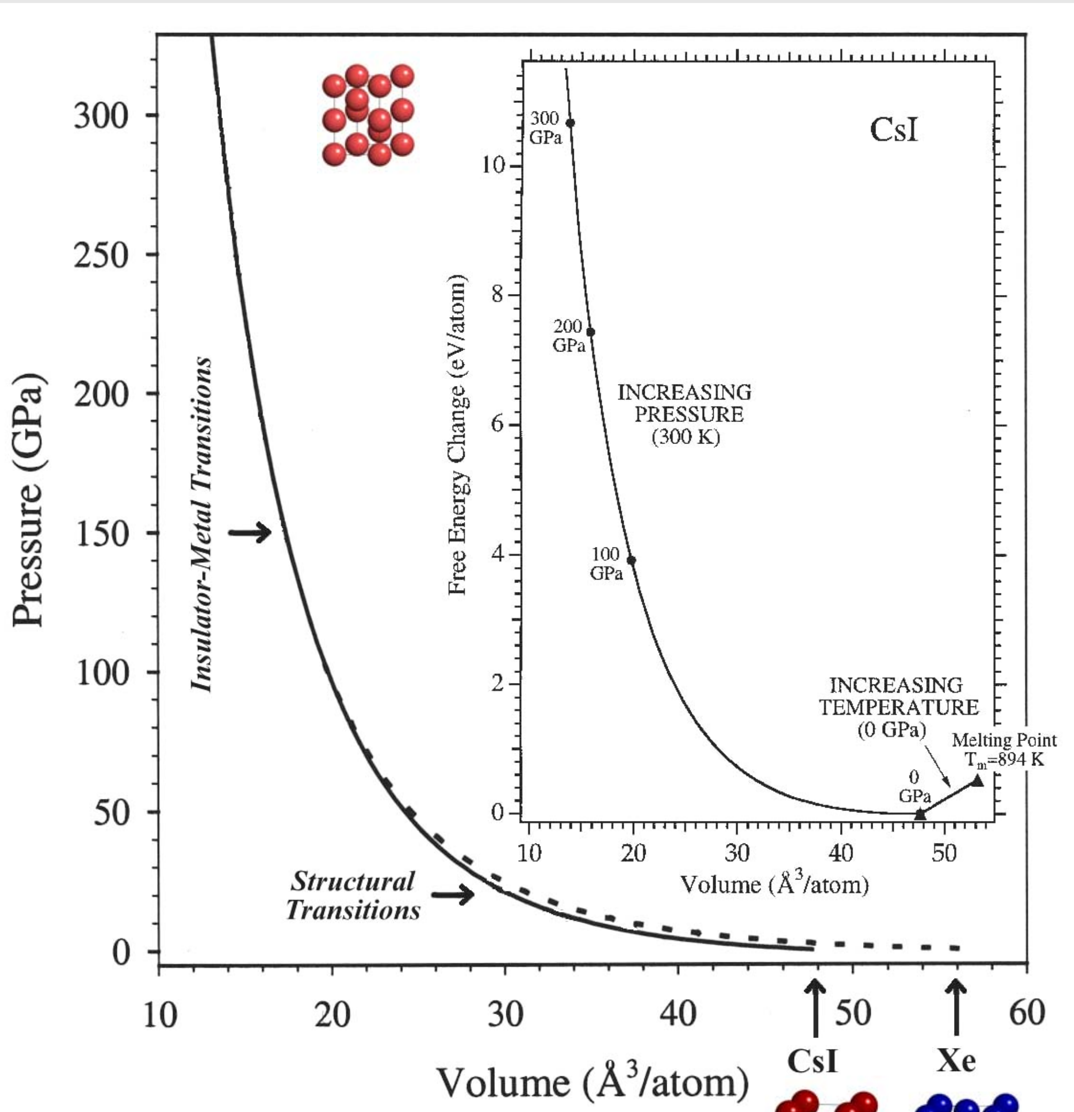
10^3 atm $\approx$ kbar
10^6 atm $\approx$ Mbar
10 kbar = 1 GPa
1 Mbar = 100 GPa

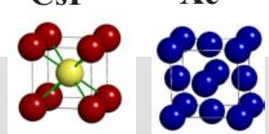
1 Gigapascal = 10^9 N/m^2





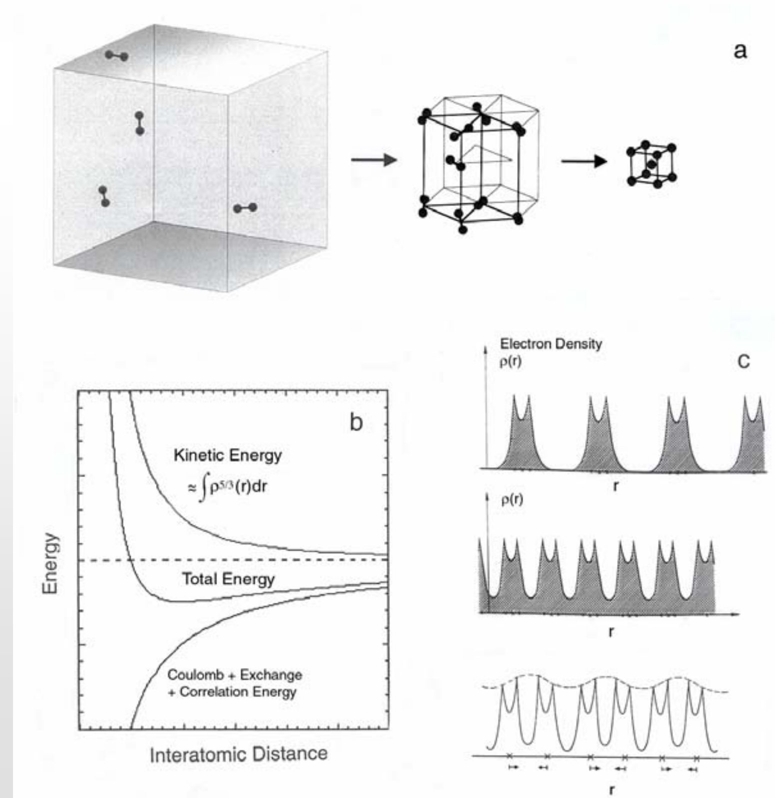
Free Energy Changes and Chemical Bonding





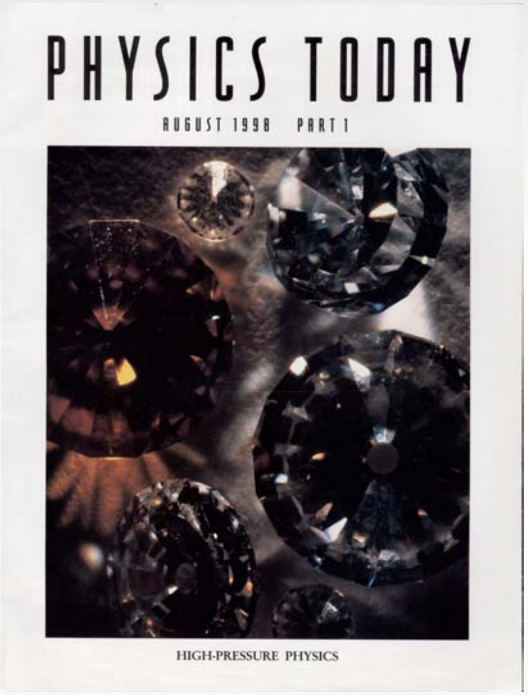
[Hemley and Ashcroft,
Physics Today 51, 26 (1998)]

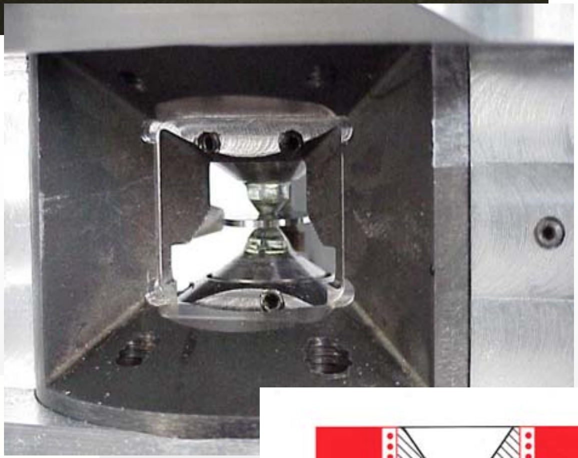
- *P-V* work can exceed binding energies
- Dramatic changes in bonding and electronic states
- Stored energy in metastable phases

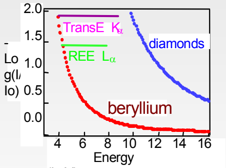


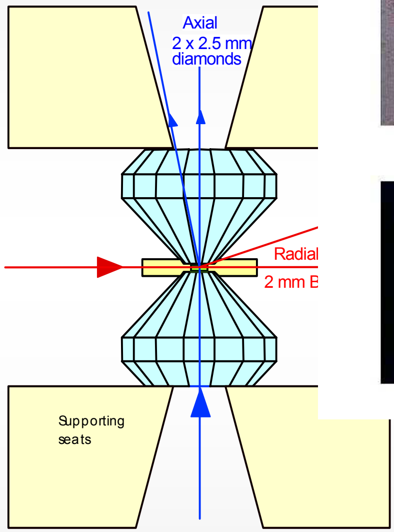
HIGH-PRESSURE TECHNOLOGY

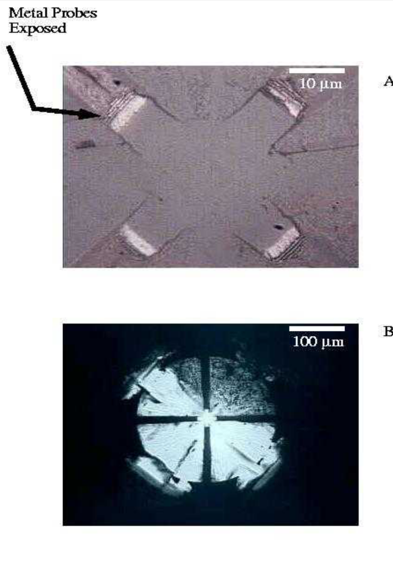
Plethora of New Instruments

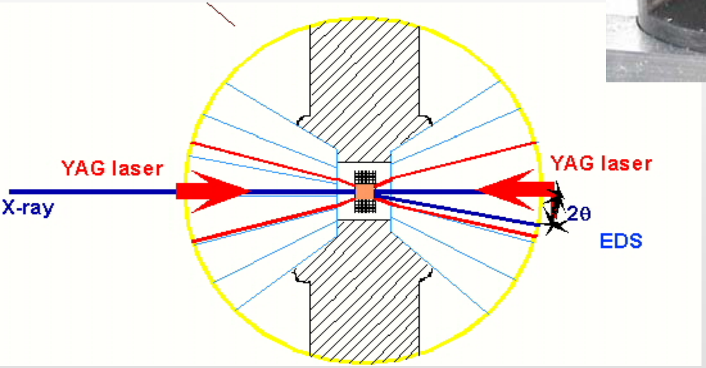


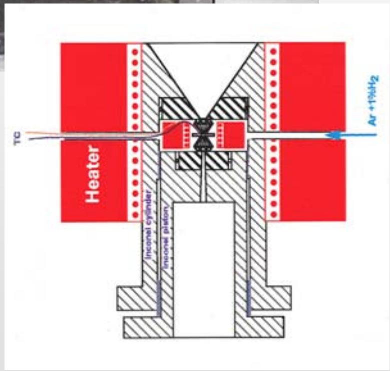


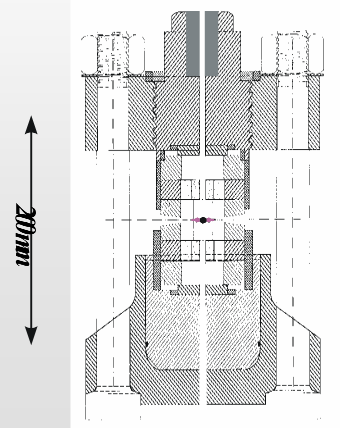




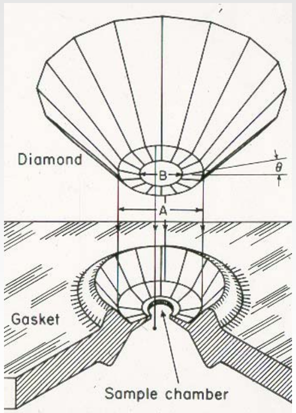








Synchrotron Infrared Spectroscopy and High Pressure



d

P	*d*
50 GPa	~200 μm
300 GPa	<10 μm

U4IR: 1990-1992

- *First megabar synchrotron IR measurements*

U2B: 1992-1998

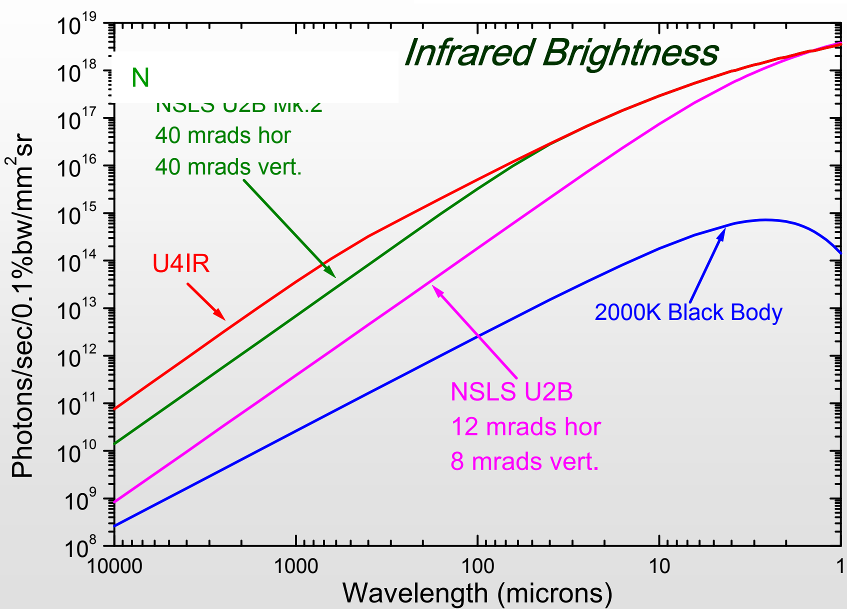
- *PRT with NSLS, Northrup Grumman*
- *Nicolet 750; custom built microscopes*

U2A: 1998-

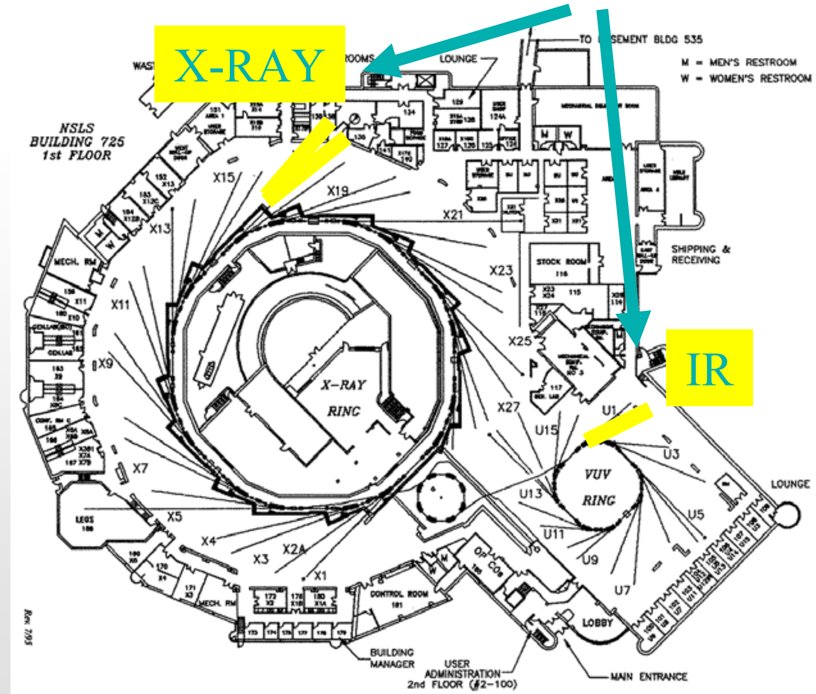
- *PRT with NSLS*
- *Integrated optical/IR spectroscopy facility*

U2A: 2004-

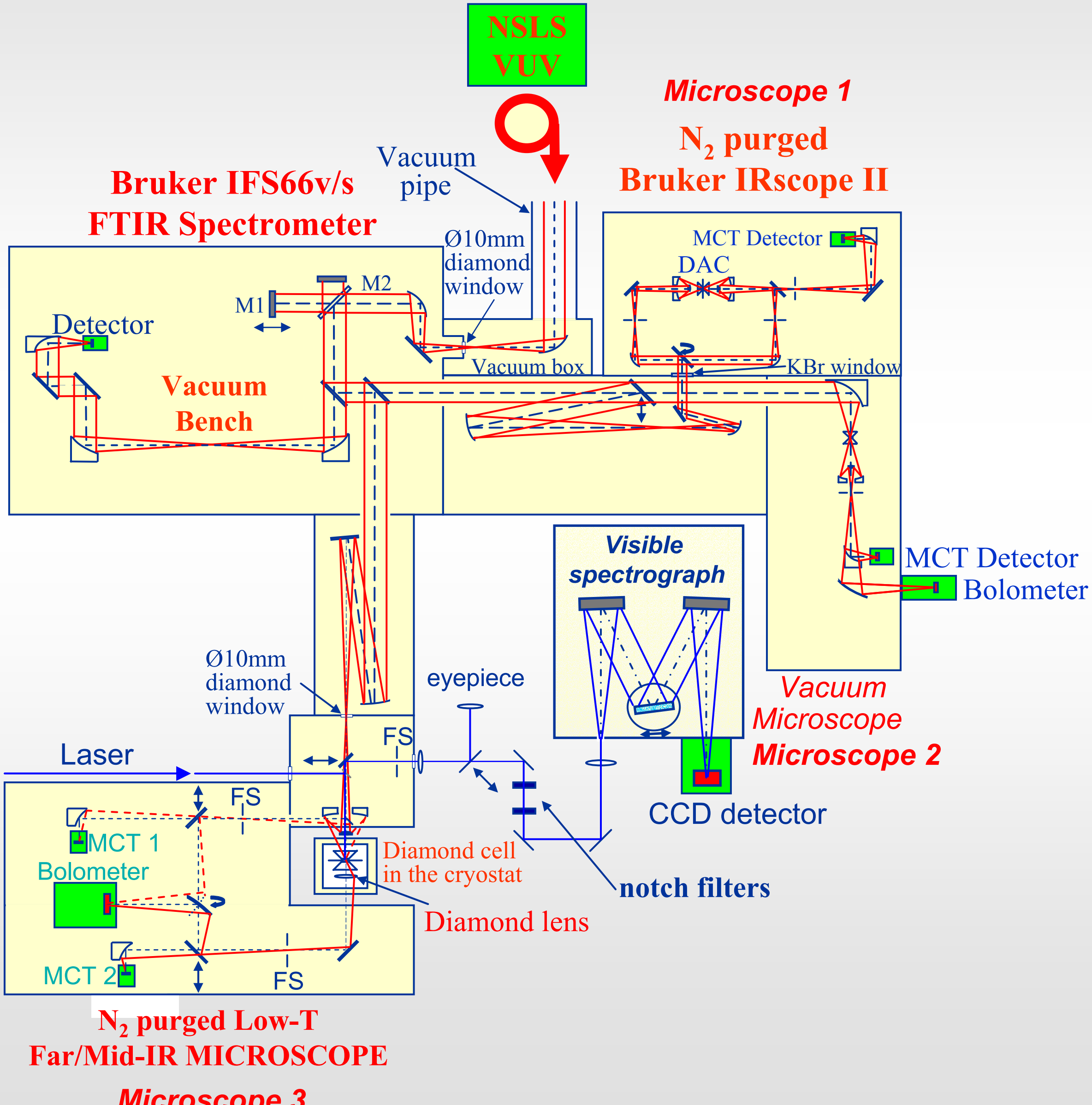
- *Improved beam delivery*
- *Far-IR enhancement*



High-Pressure Beam lines



U2A Beamline Upgrade:
IMPROVED FAR-IR AND BEAM DELIVERY

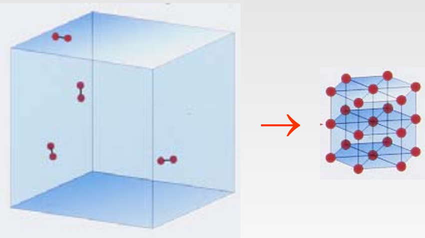


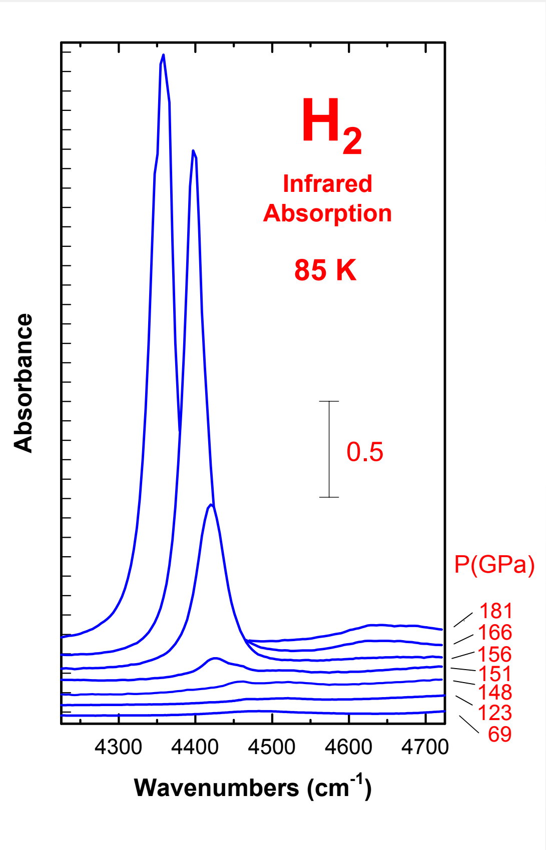
- Near IR through far IR spectral range
- Reflectivity and absorption measurements
- Low-temperature measurements
- Mapping of the samples
- *In situ* Raman and fluorescence measurements
- Diamond lens
- Small diamonds

A WEALTH OF FINDINGS:

1. Condensed Matter Physics

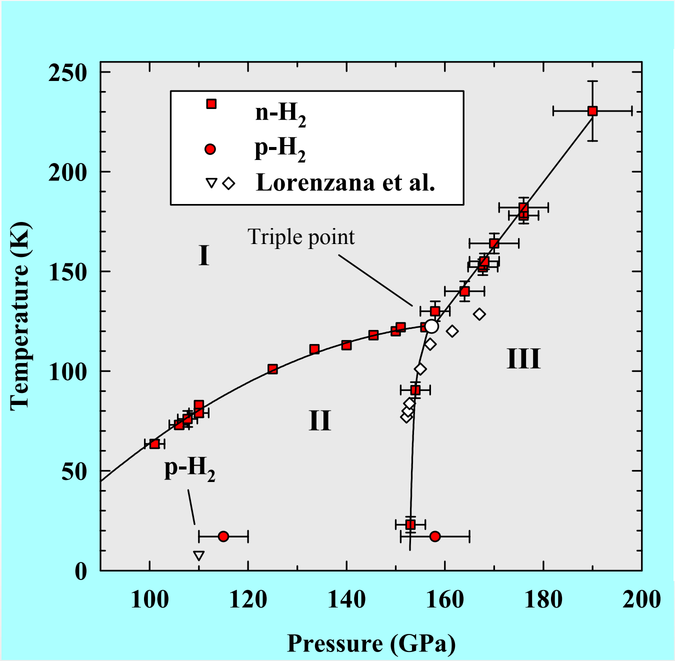
- HYDROGEN AT MEGABAR PRESSURES





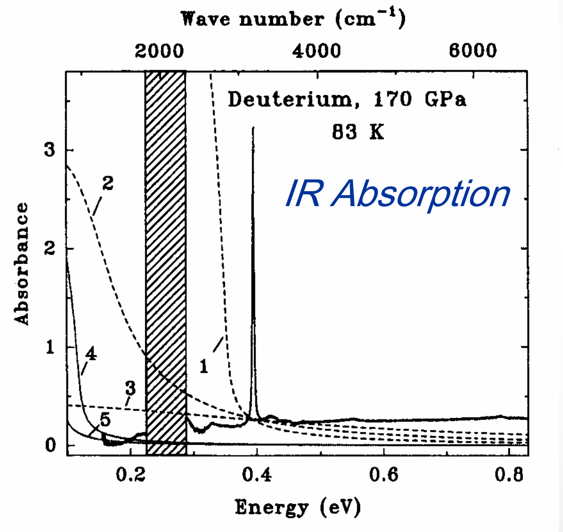
ANOMAIOUS
CHARGE TRANSFER STATE

[Hemley *et al., Nature* **369**, 384 (1994)]



UNEXPECTED PHASE DIAGRAM

[Mazin *et al., Phys. Rev. Lett.* **78**, 1066 (1997);
Goncharov *et al., ibid.* **75**, 2514 (1996);
Lorenzana et al., *ibid.*, **63**, 2080 (1989)]



NO "MOLECULAR" METALLIZATION (to 230 GPa)

[Hemley *et al., Phys. Rev. Lett.* **76**, 1667 (1996); Chen et al. *Phys. Rev. Lett.* **76**, 1667 (1996)]

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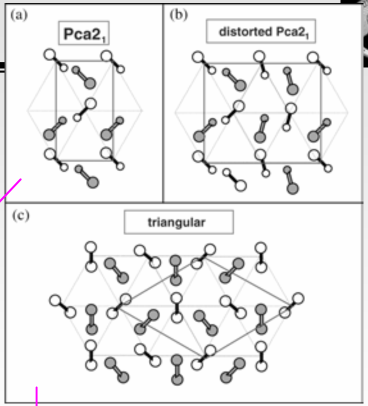
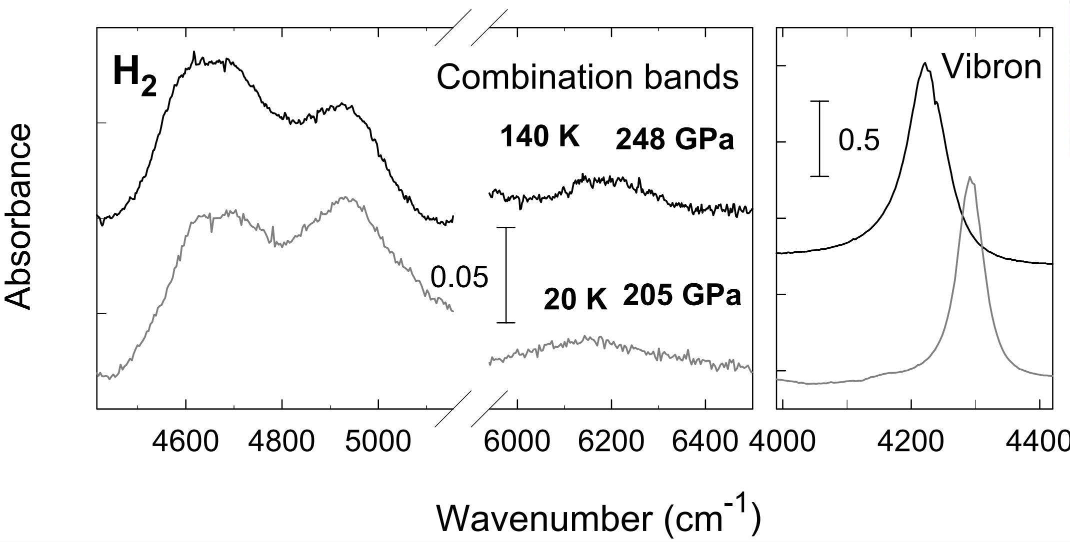
A WEALTH OF FINDINGS:

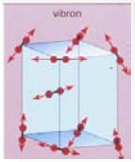
1. Condensed Matter Physics

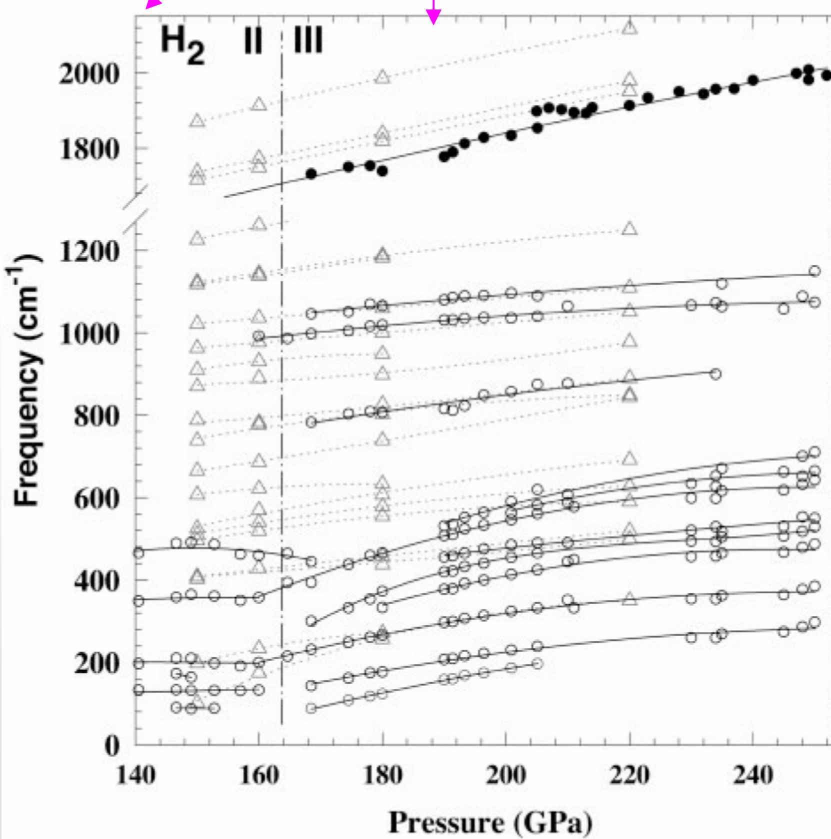
Multimegabar Vibrational Spectroscopy

[Kohanoff *et al.*, *Phys. Rev. Lett.* 83, 4097 (1999)]









[Goncharov *et al.*, *Proc. Nat. Acad. Sci.* 98, 14234 (2001)]

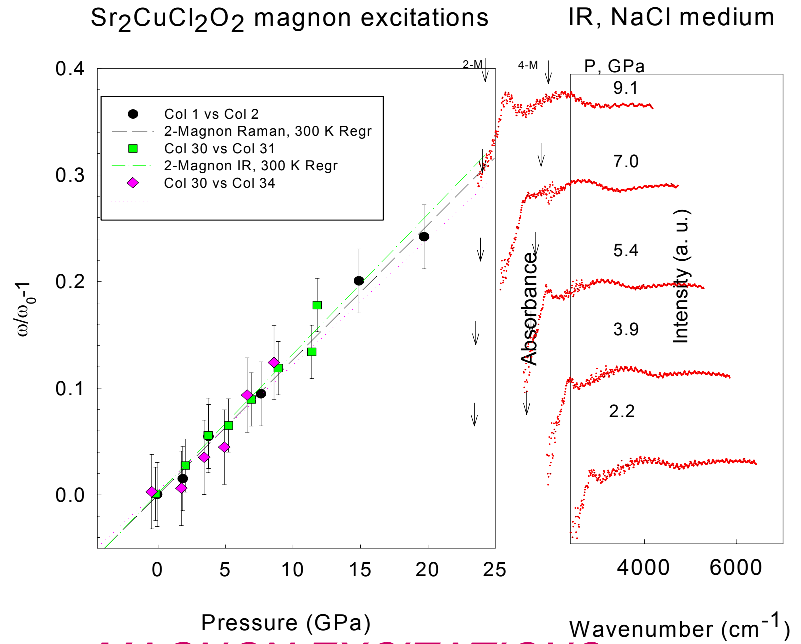
- Molecules stable to 300 GPa in solid
- Constraints on the crystal structure

A WEALTH OF FINDINGS:

1. Condensed Matter Physics

- *INFRARED EXCITATIONS IN HIGH-Tc SUPERCONDUCTORS*

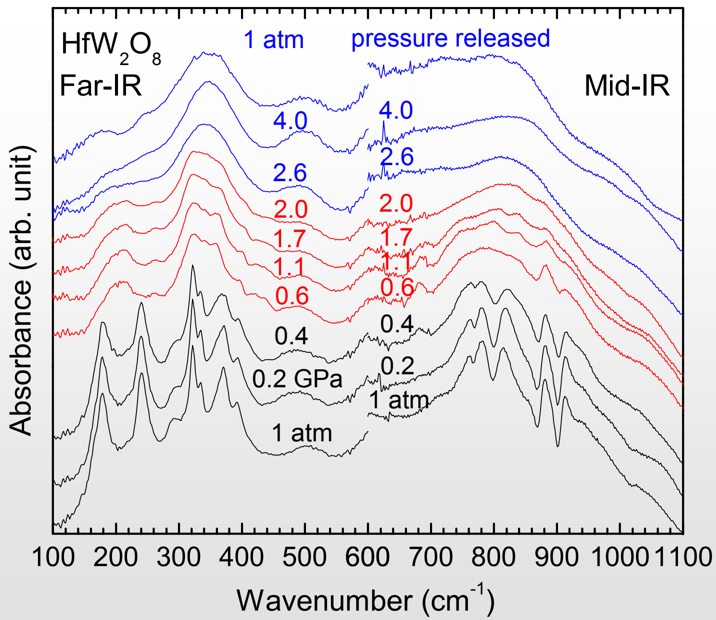
[Struzhkin *et al. J. Phys. Condens. Matter, in press*]



- *MAGNON EXCITATIONS*

[Struzhkin *et al., Phys. Rev. B* 62, 3895 (2000)]

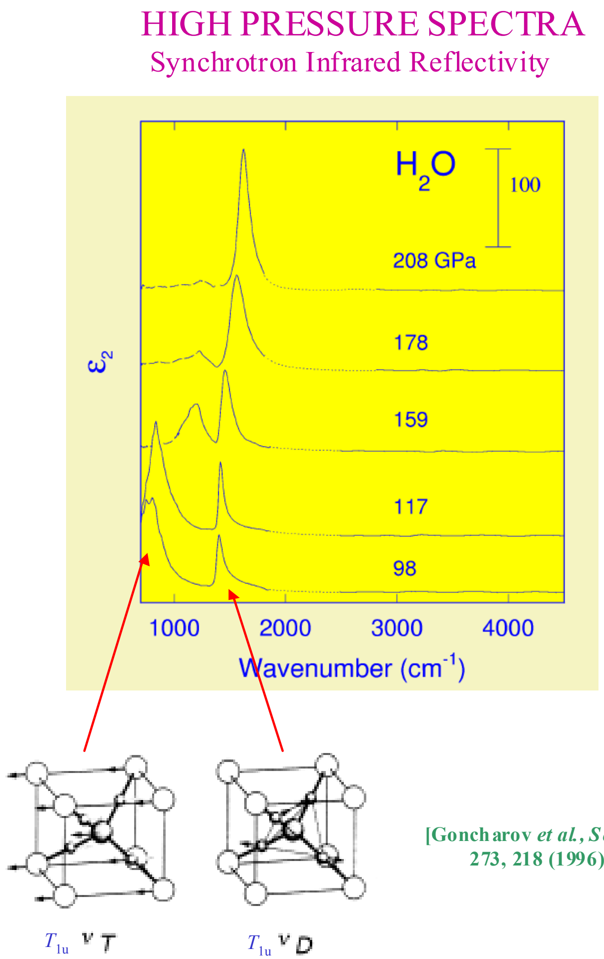
- *NOVEL TRANSFORMATIONS*



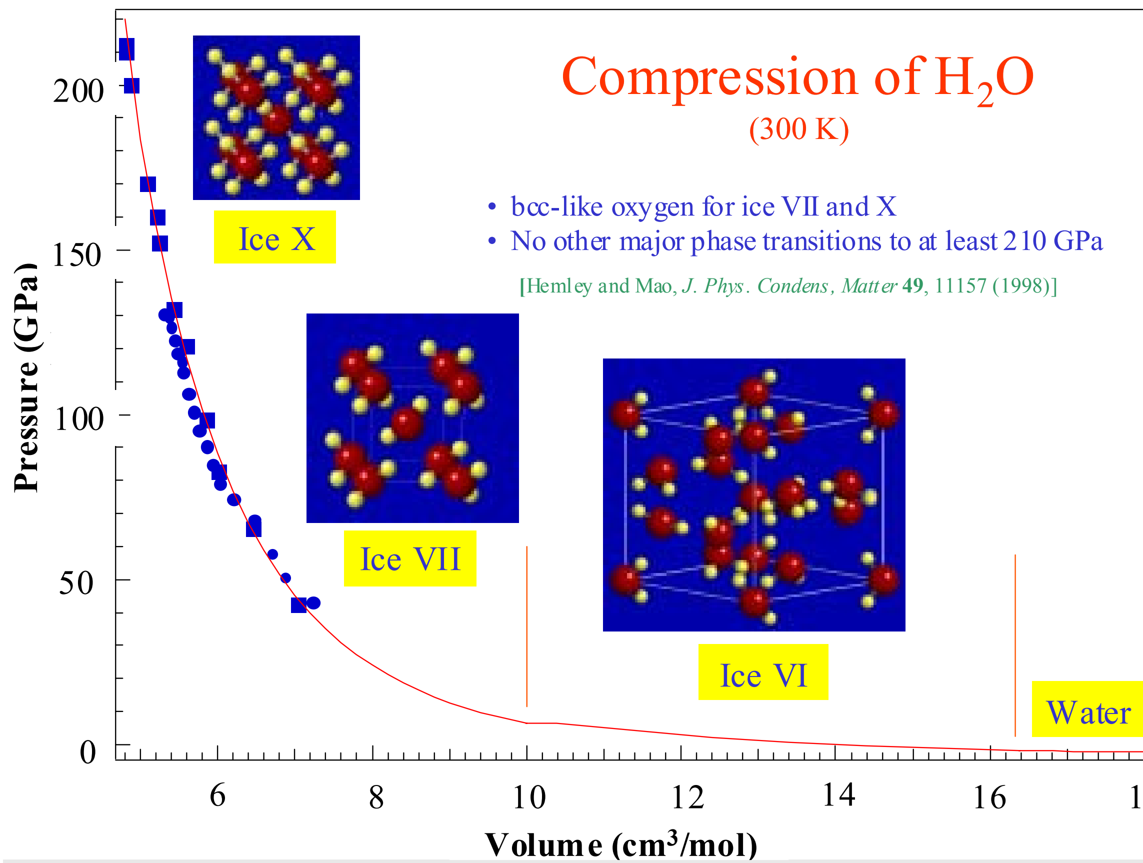
Pressure-induced amorphization of HfW_2O_8

[Chen *et al. Phys. Rev. B* 64, 20040 (2002)]

A WEALTH OF FINDINGS:
2. Chemistry



[Goncharov *et al.*, *Science* 273, 218 (1996)]

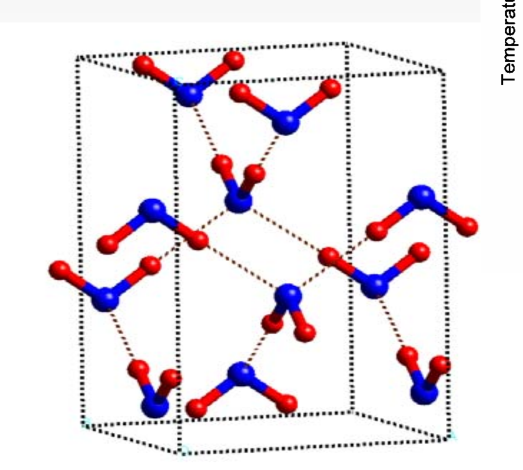


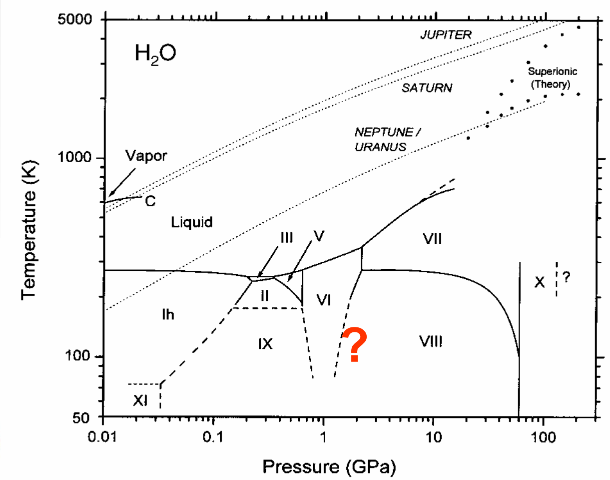
- Non-molecular ice identified by IR reflectivity above 60 GPa
- X-ray Confirms spectroscopic data: bcc-based structure

A WEALTH OF FINDINGS:

2. Chemistry

- *ANOMALOUS TRANSITIONS IN ICE VIII*





78, NUMBER 16 PHYSICAL REVIEW LETTERS 21 APRIL 1997

Structural Instability in Ice VIII under Pressure

J. M. Besson and S. Klotz

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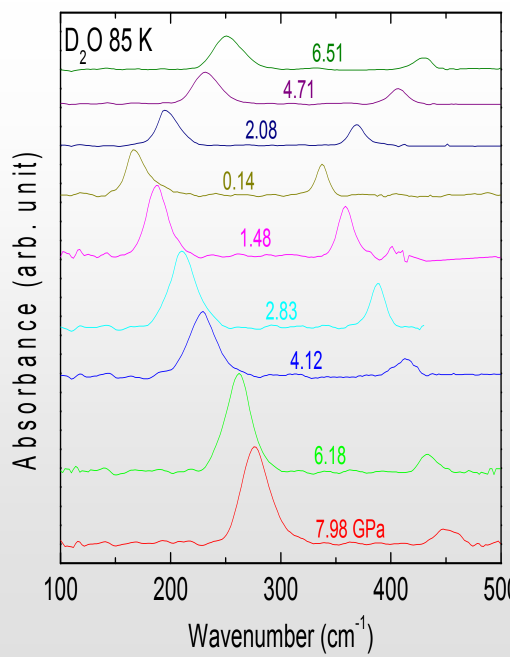
G. Hamel

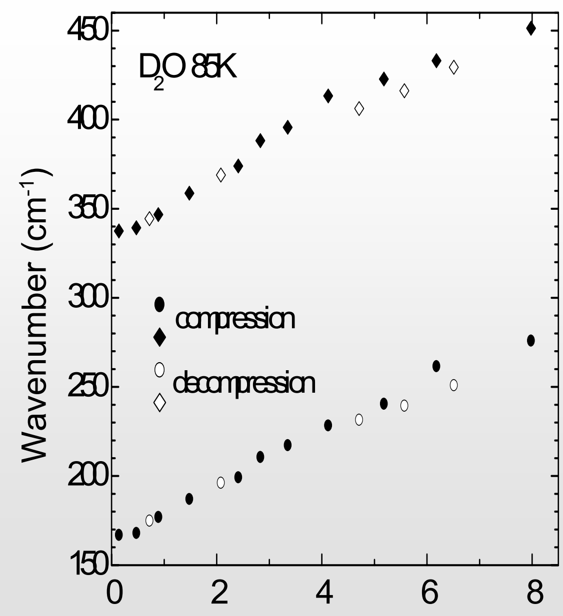
partement des Hautes Pressions, Université Pierre et Marie Curie, B73, 4, Place Jussieu, F-75252, Paris, France

W. G. Marshall, R. J. Nelmes, and J. S. Loveday

Department of Physics and Astronomy, The University of Edinburgh, Edinburgh EH9 3JZ, United Kingdom

(Received 26 September 1996)





Pressure dependence of IR translational and rotational mode frequencies in D_2O → *No transition*

[Klug *et al., Phys. Rev. Lett., submitted*]

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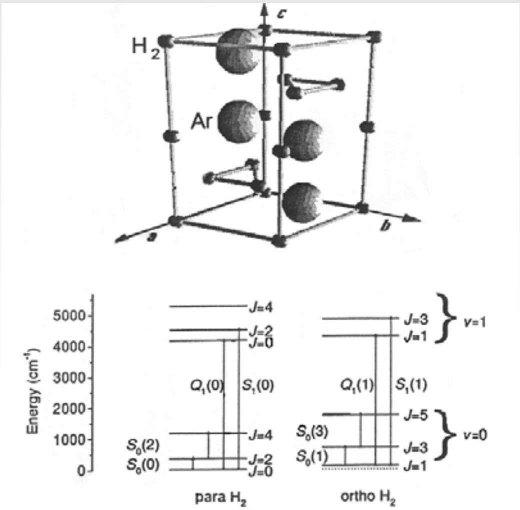
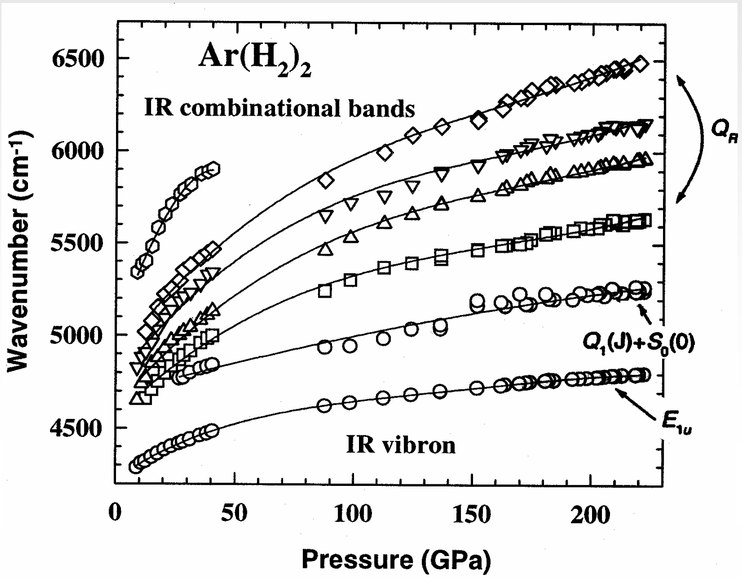
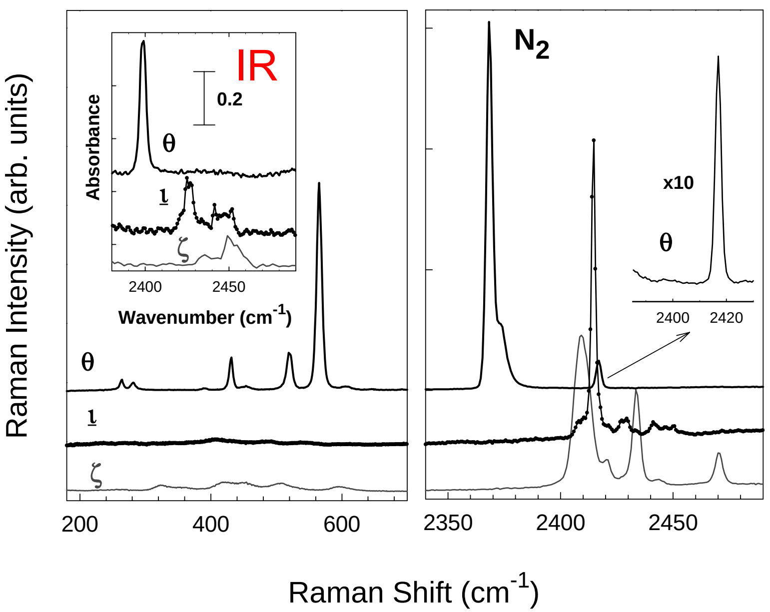
A WEALTH OF FINDINGS:
2. Chemistry

- VAN DER WAALS COMPOUNDS

[Loubeyre *et al.* (1994); Datchi *et al.* (1997); Hemley (2000); Ulivi *et al.* (2001)]

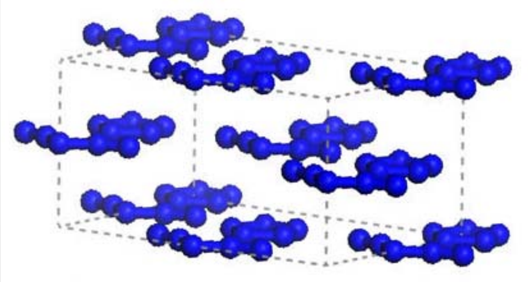






- NOVEL MOLECULAR PHASES

- Quenchable to 300 K
- Polynitrogen: *e.g.*, $N_5^+ N_5^-$



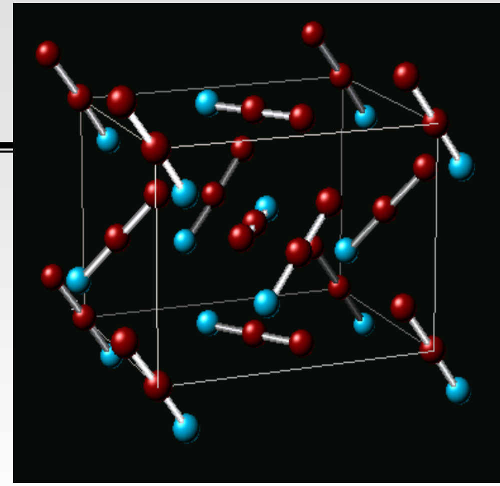
A WEALTH OF FINDINGS:

2. Chemistry

- *NOVEL MOLECULAR PHASES*

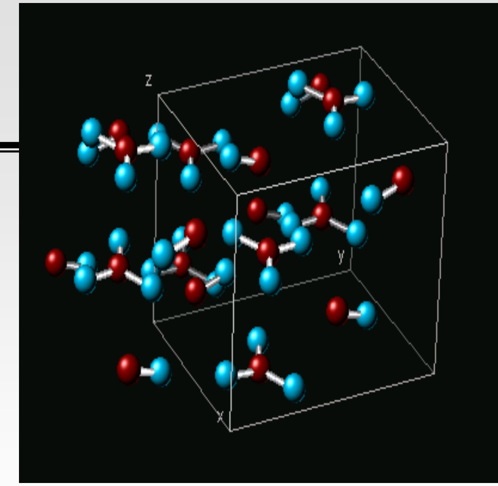
- NO^{+}-NO_3^{-}: an unusual ionic phase probed by far-IR and x-ray

β-N_2O

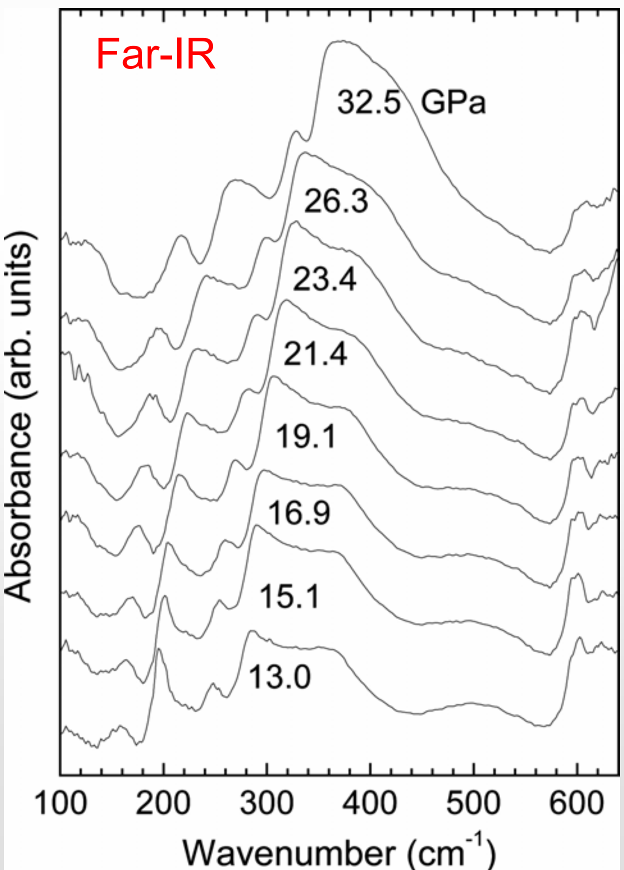


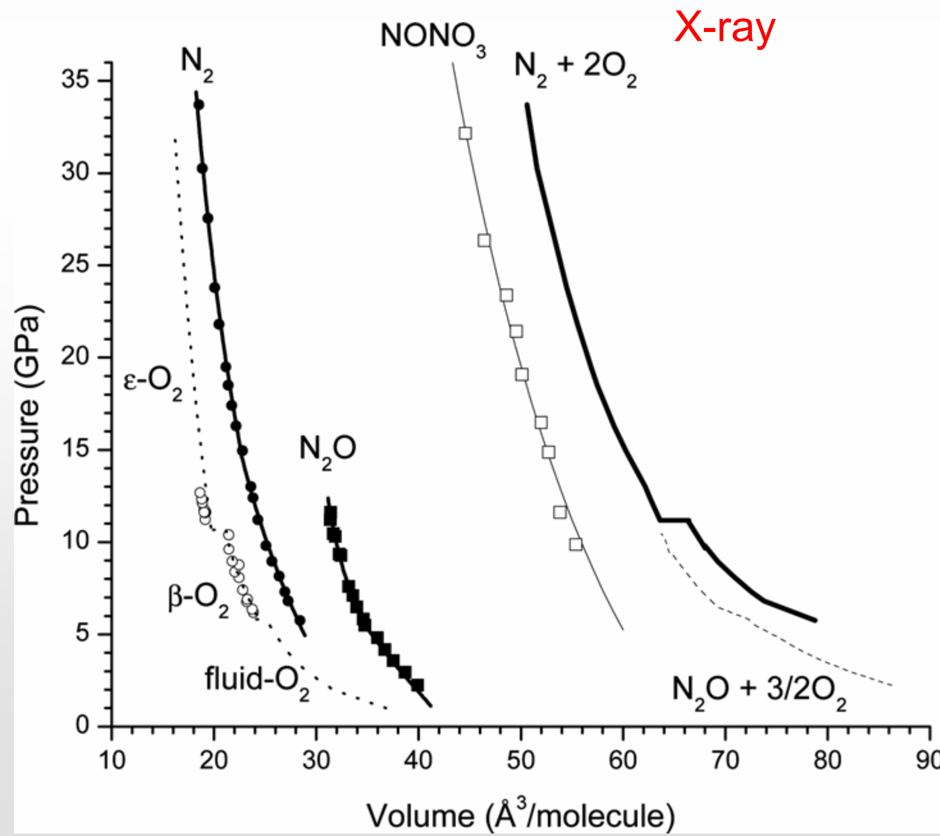
→

NO^{+}-NO_3^{-}



[Somayazulu *et al.*, *Phys. Rev. Lett.* 87, 135504 (2001); Song *et al.* 119, 2232 (2003)]

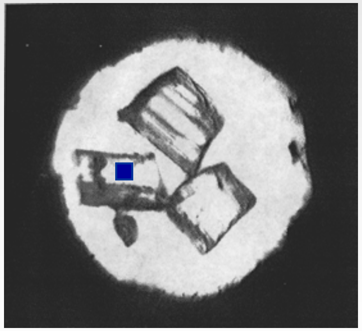




A WEALTH OF FINDINGS:
3. Earth and Planetary Science

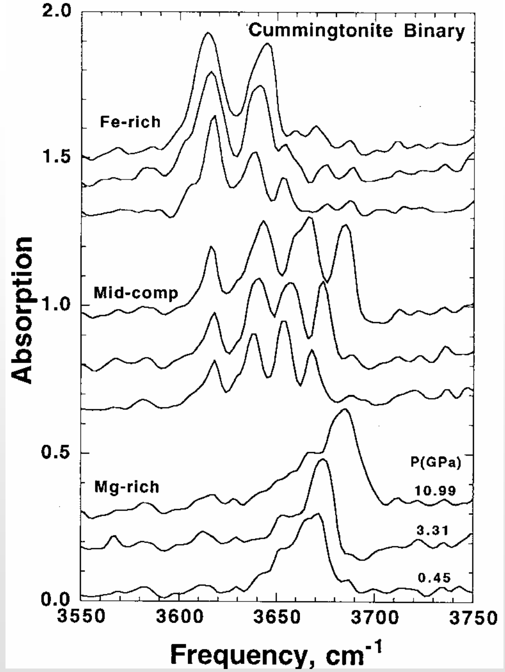
In Situ Measurements:
MULTIPLE CRYSTALS

- *VIBRATIONAL PROPERTIES*
  (Transition mechanisms and thermodynamic properties)
- *INSULATOR-METAL TRANSITIONS*
- *MICROSPECTROSCOPY OF INCLUSIONS*
- *DENSE SILICATES IN THE MANTLE*



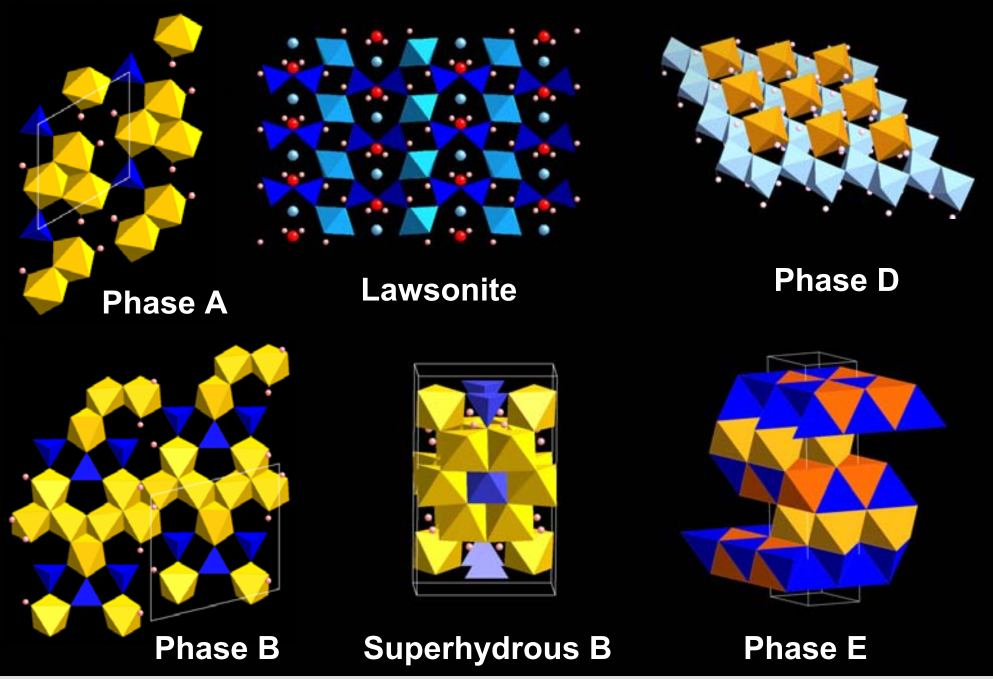
200 μm

Displacive transformation in cummingtonite



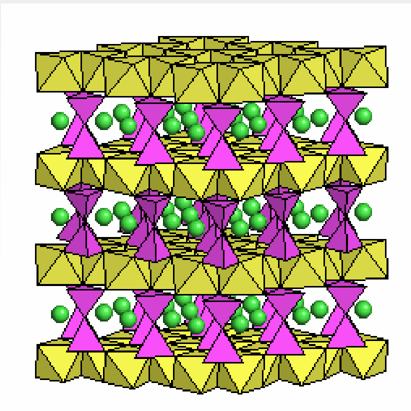
[Yang *et al.*, *Am. Mineral.* 83, 288 (1998)]

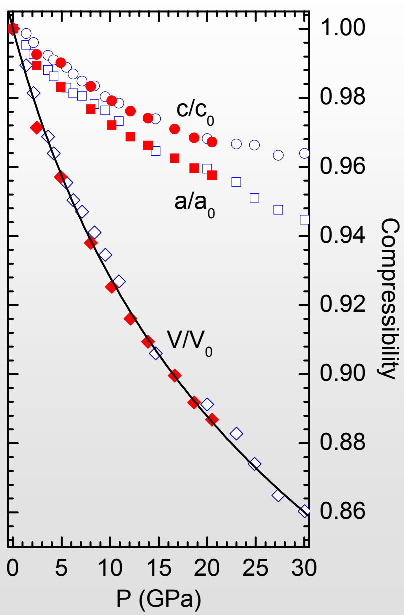
HYDROUS PHASES IN THE DEEP MANTLE:
Hydrogen Incorporation in Dense Silicates

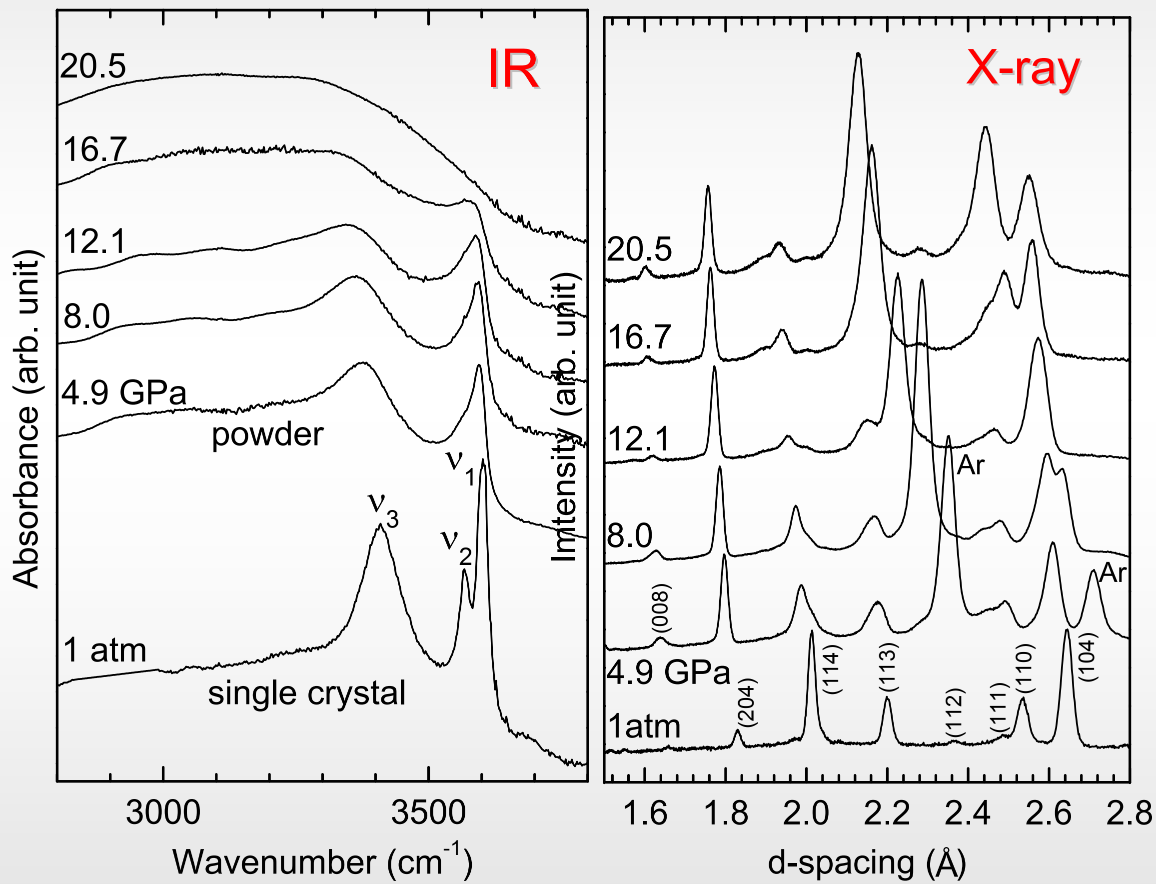


A WEALTH OF FINDINGS:
3. Earth and Planetary Science

High-Pressure Behavior of $K_{1.54}Mg_{1.93}Si_{1.89}O_7H_{1.04}$





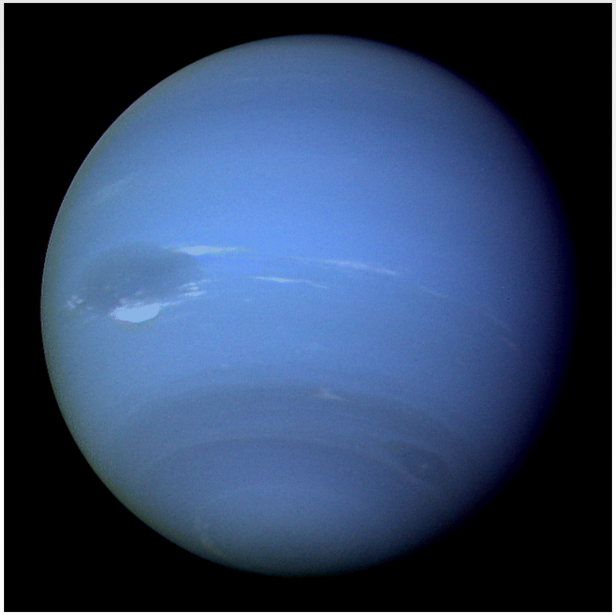


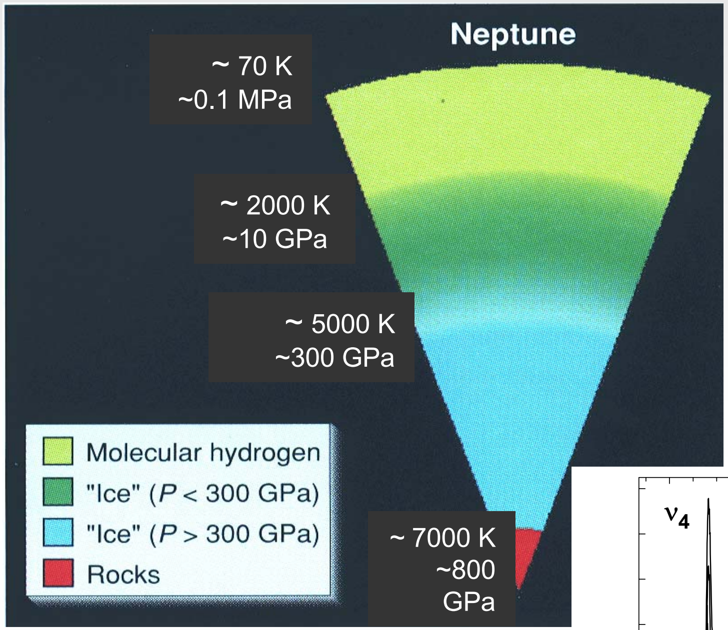
- H disordering above ~15 GPa
- Crystalline-crystalline transformation

[Liu *et al. J. Phys.: Condens. Matter* 14, 1064 (2003)]

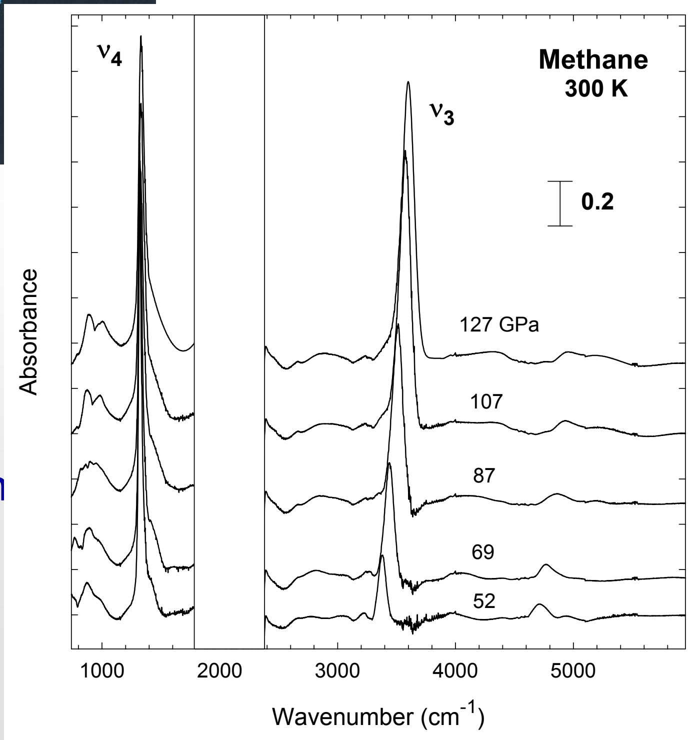
A WEALTH OF FINDINGS:

3. Earth and Planetary Science





IR Absorption



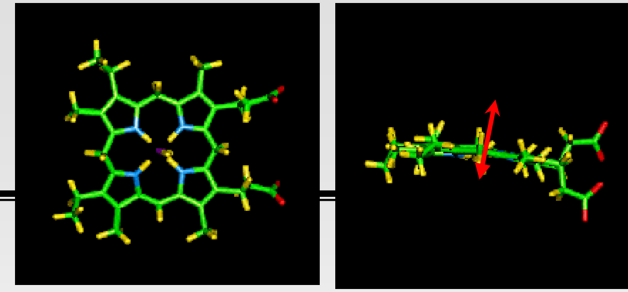
- Hydrocarbon stability to megabar pressure
  300 K compression
- Consistent with powder and single-crystal diffraction
- New physics (H-rich alloy)?

- PLANETARY GASES AND ICES

[Badro *et al., to be published*]

A WEALTH OF FINDINGS:

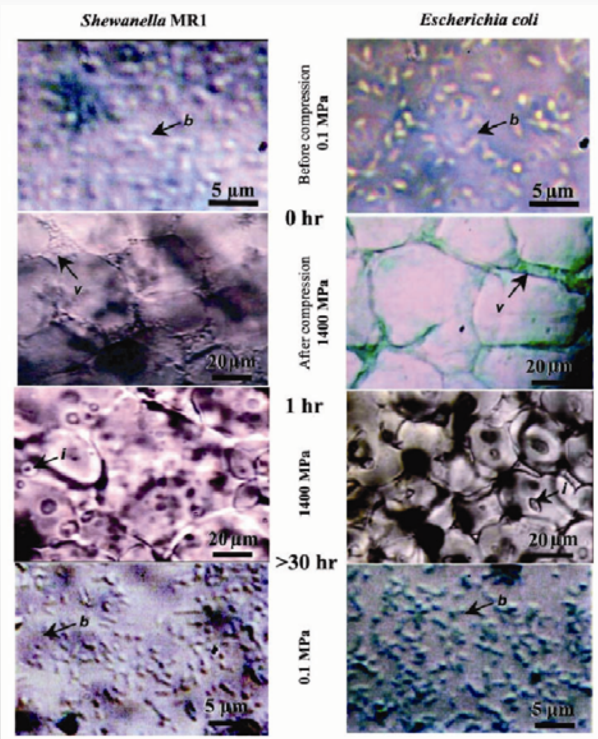
4. Biology and Soft Matter



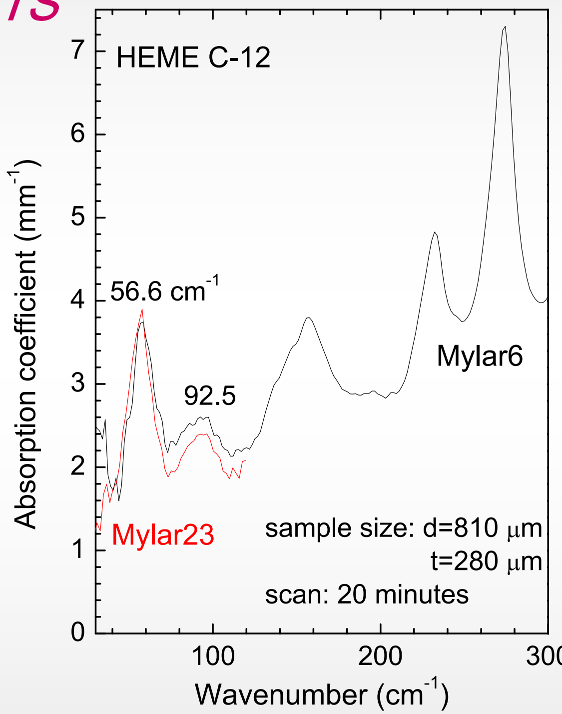
HEME DOMING-MODE

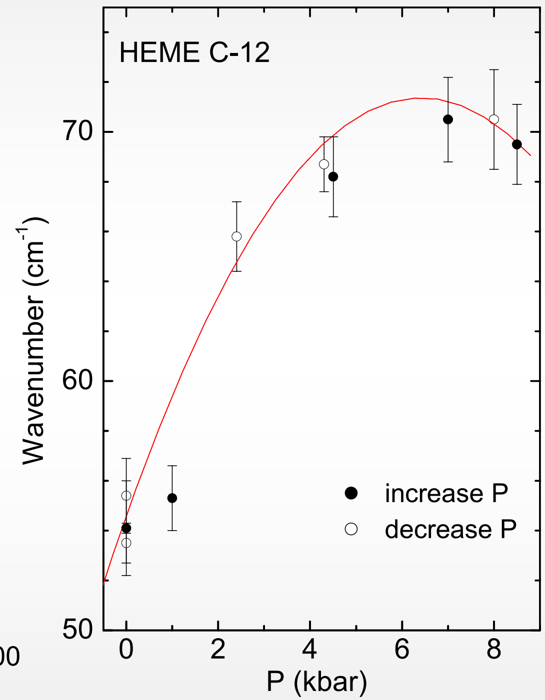
- BIOCHEMICAL REACTIONS IN HYDROTHERMA FLUIDS

- LIFE IN EXTREME ENVIRONMENTS (>1600 MPa)



[Sharma *et al.*, *Science* 295, 1514 (2002)]





- BIOMOLECULE VIBRATIONAL DYNAMICS

[Klug *et al.*, *Proc. Nat. Acad. Sci.* 99, 12526 (2002)]

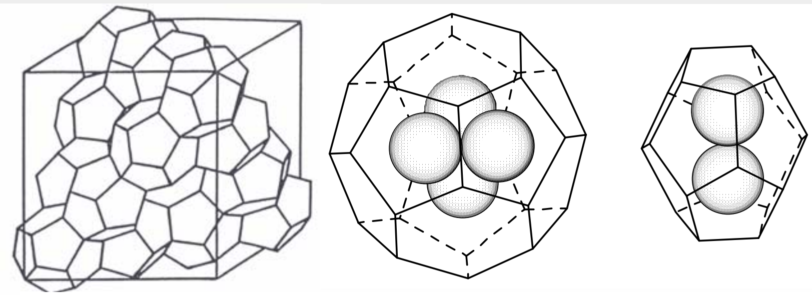
- **Doming mode found at 57 cm^{-1}**
- **Far-IR at high pressure**

Carnegie Institution

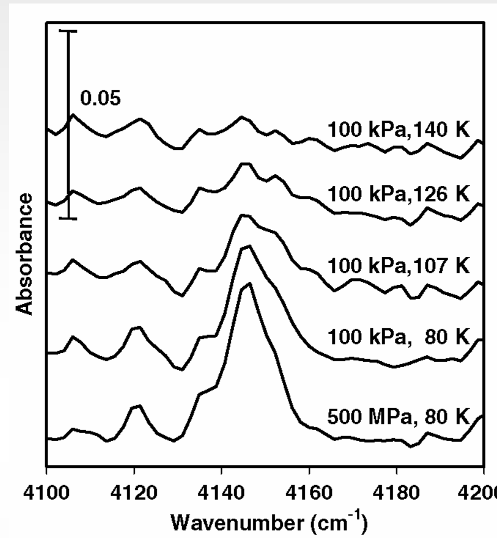
A WEALTH OF FINDINGS:

5. Materials Science and Technology

- *SUPERHARD MATERIALS* [Zhao *et al*., *J. Mat. Sci., in press*]
- *HYDROGEN STORAGE MATERIALS*

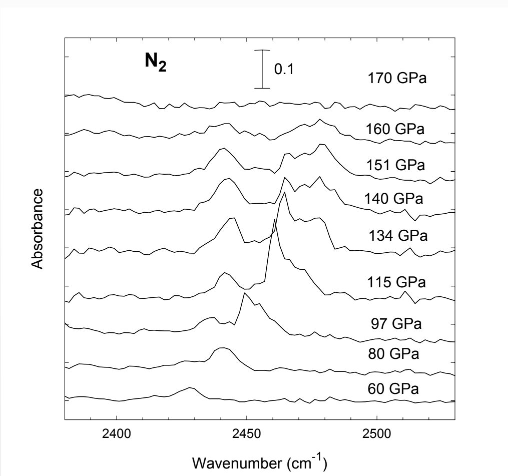


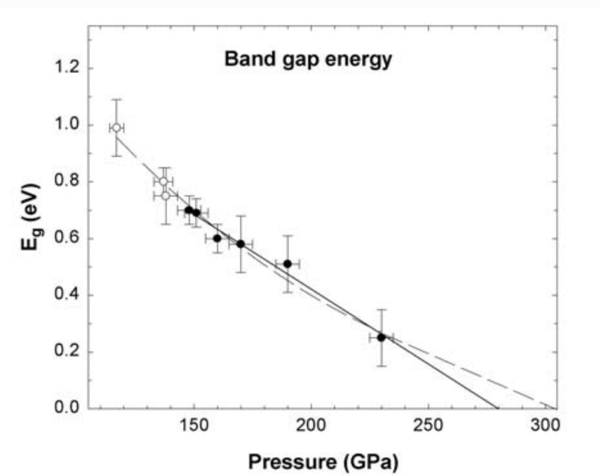
Novel H_2-H_2O structure II clathrate
Stable at ambient pressure to 145 K
5.3 % hydrogen (4.5 % DOE 2005 target)

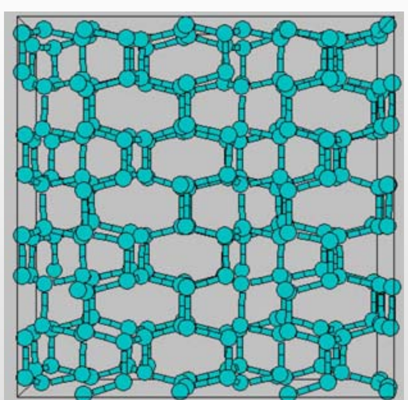


[W. Mao *et al*. *Science* 297, 2247 (2002)]

- *HIGH ENERGY DENSITY MATERIALS*







NITROGEN DISSOCIATION *SEMICONDUCTING BEHAVIOR*

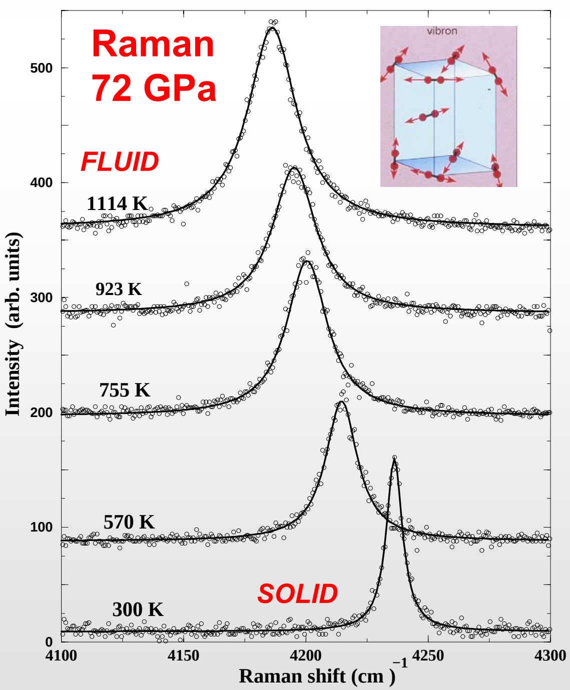
[Goncharov *et al*., *Phys. Rev. Lett*. 85, 1262 (2000); Eremets *et al. Nature* 411, 170 (2001)]

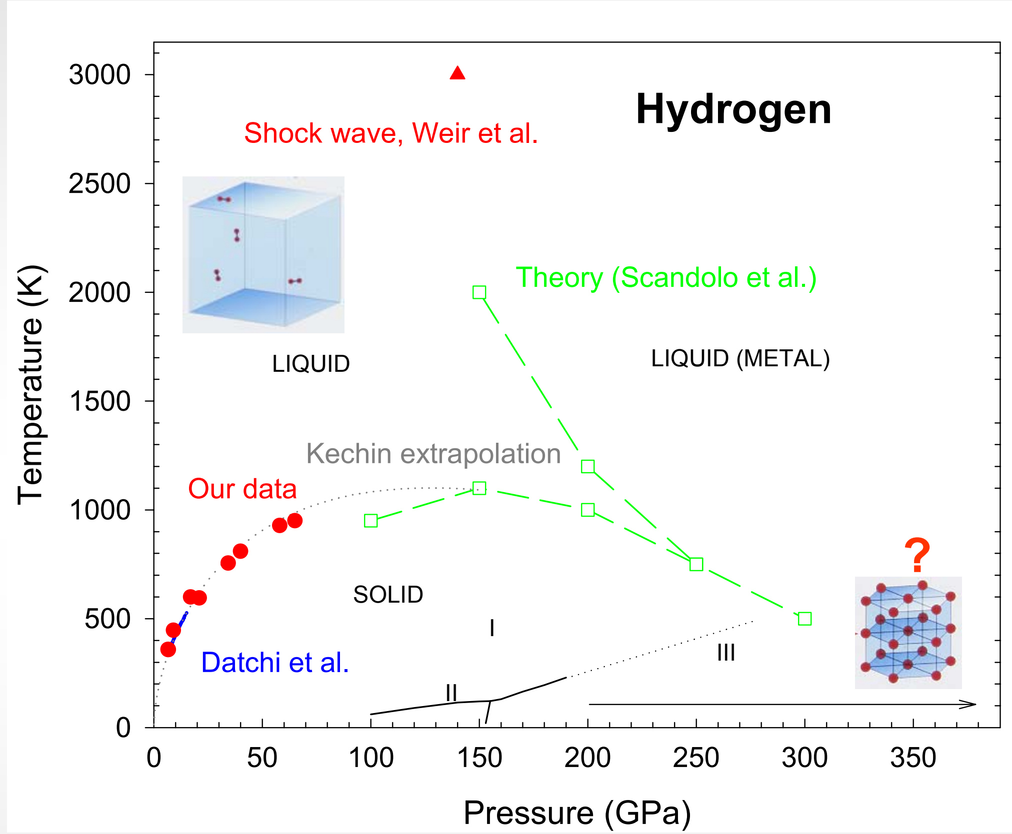
OPPORTUNITIES AND CHALLENGES

- Higher pressures and temperatures
  - *physics/chemistry/astrophysics/planetary science*
- Higher precision/acccuracy/sensitivity
  - *all pressure ranges*
- Broader wavelength range
  - far-IR, THz
- Time resolution
  - *transition kinetics to chemical dynamics*
- Integration of techniques
  - *diffraction, inelastic scattering, imaging*
- New generation of instrumentation
  - *large volume, smart anvil cell designs*

OPPORTUNITIES AND CHALLENGES:

Grand Challenge of Hydrogen at Extreme P-T





- **Liquid ground state?**
- **High-T_c superconductor?**
- **Higher *P-T* needed**
- **Infrared combined with x-ray inelastic scattering phonons/electrons**

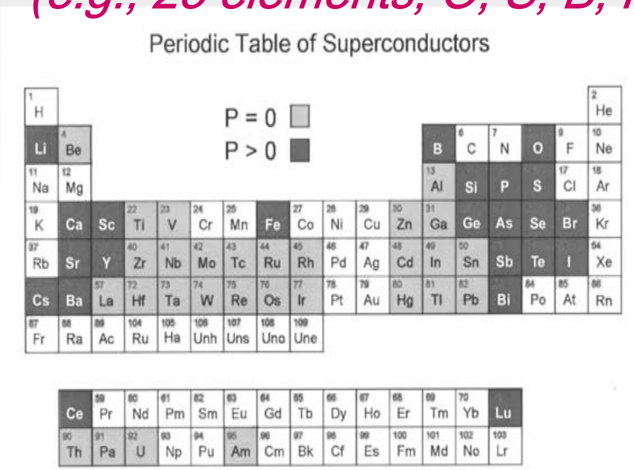
[Gregoryanz *et al.*, *Phys. Rev. Lett.* 90, 175701 (2003)]

OPPORTUNITIES AND CHALLENGES:

Electronic Structure, Bonding, Synthesis of Novel Materials

-NOVEL SUPERCONDUCTORS

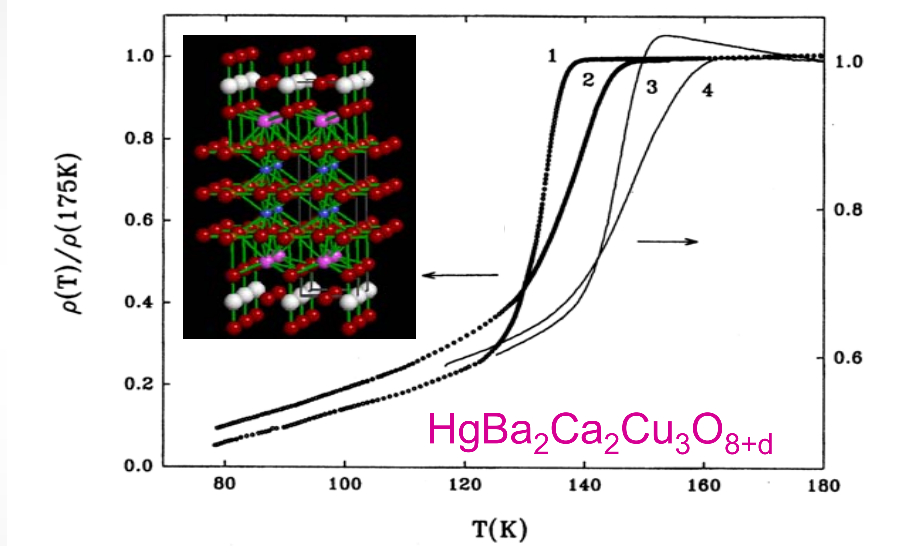
(e.g., 23 elements; O, S, B, Fe, Li)



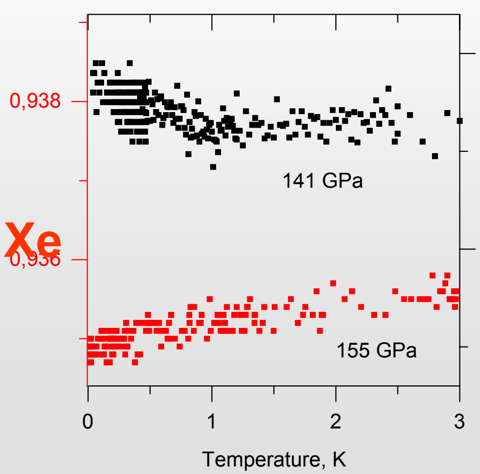
[Struzhkin *et al.* (2002)]

- HIGHEST TEMPERATURE SUPERCONDUCTIVITY

T_c = 164 K at 30 GPa **[Gao et al. (1994)]**



- EXCITONIC INSULATOR STATES?



[Eremets *et al.* (2000)]

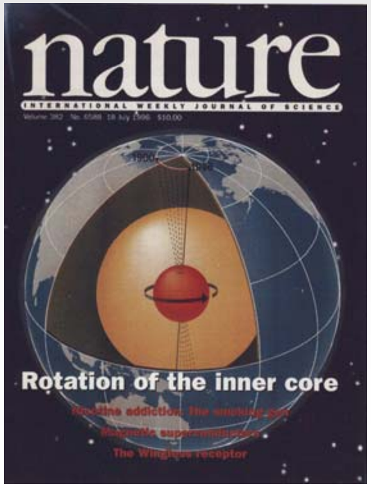
Electrical Resistivity to 27 mK and 160 GPa

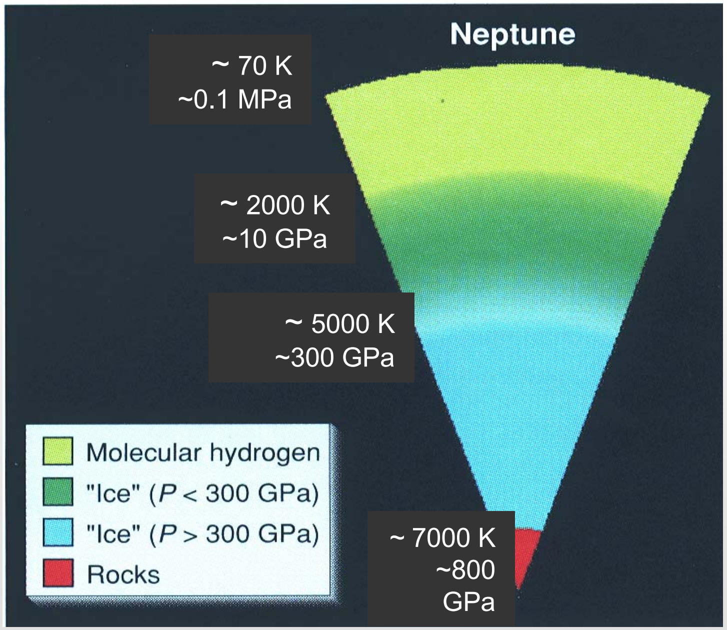
- **Integrated studies to >300 GPa and to millikelvin temperatures**
- **Far-IR to optical range**
- **Combined with x-ray inelastic scattering phonons/electrons**
- **Recovery to ambient**

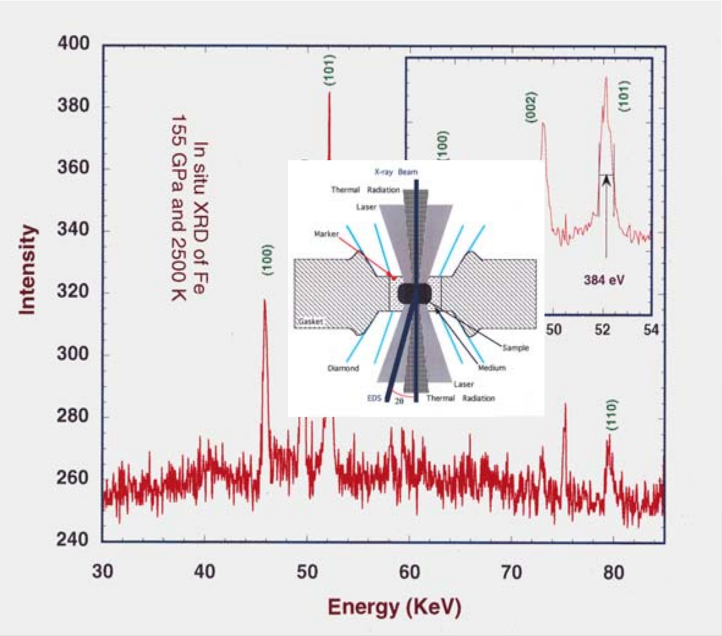
OPPORTUNITIES AND CHALLENGES:

Spectroscopy of Earth Materials at Extreme P-T

- *NATURE OF THE CORE FROM IN SITU OPTICAL STUDIES*
- *CHEMICAL REACTIONS IN THE DEEP EARTH*
- *HYDROCARBON STABILITY AND ENERGY RESOURCES*
- *IN SITU HIGH P-T STUDIES OF PLANETARY GASES AND ICES*



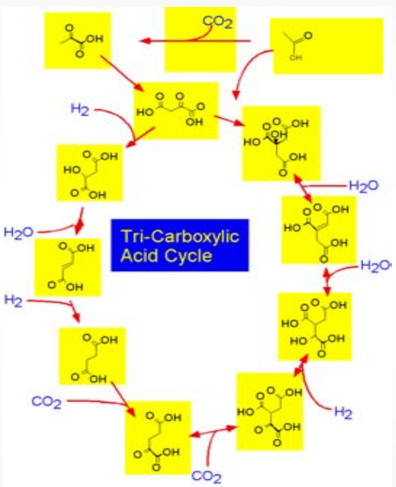


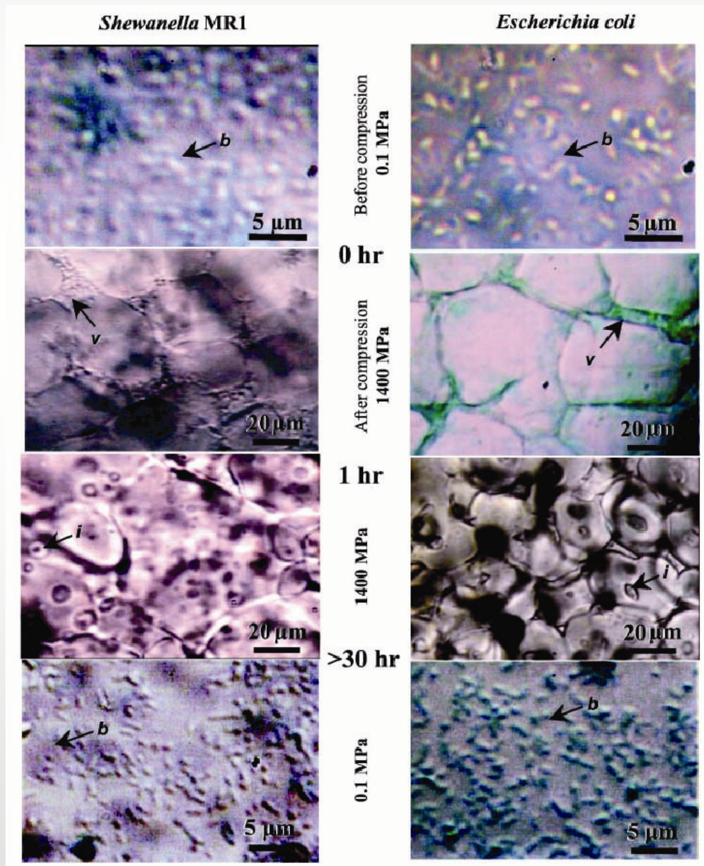


OPPORTUNITIES AND CHALLENGES:

Life in Extreme Environments and Origin of Life

- *BIOCHEMICAL REACTIONS*
- *HIGH-PRESSURE MICROBIOLOGY*





- **IR/optical/x-ray imaging with *P-T-t***
- **Single cells under stress**
- **"Test-tube" study of microbial evolution and adaptation**
- **Combined with other probes in new instrumentation**

[Sharma *et al.*, *Science* 295, 1514 (2002)]

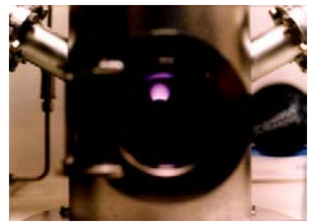
OPPORTUNITIES AND CHALLENGES:

Towards TPa Pressures with Large Volume Anvil Cells

GOALS:

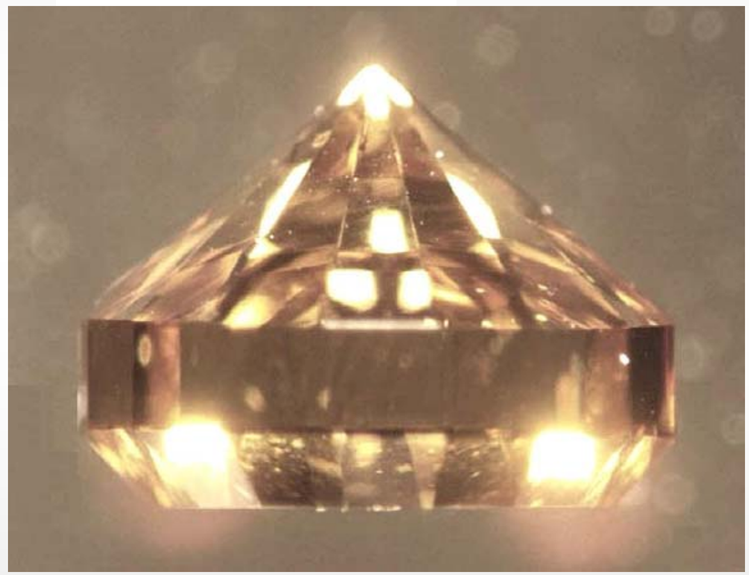
- **Higher pressures (1 TPa or 10 Mbar) and temperatures (>1 eV)**
- **Larger sample volumes needed (*e.g.*, diffraction limited far-IR)**
- **Accuracy/precision compromised**
- **Applications of several simultaneous probes limited**

Diamond Growing in a Plasma Reactor



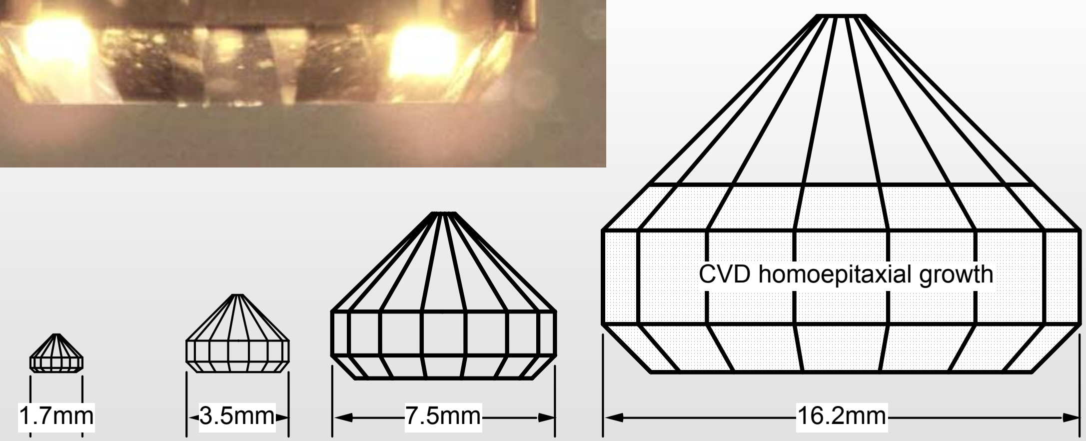
Growth of Diamond Anvils by Homoepitaxial Chemical Vapor Deposition

[Yan *et al*. *PNAS* 99, 12523 (2002)]



- 2.45 mm high
- 0.28 carats
- 0.45 mm seed
- <u>Grown in 1 day</u>

[Yan *et al*. *Phys. Stat. Sol.* 201, R27 (2004)]



Carnegie Institution

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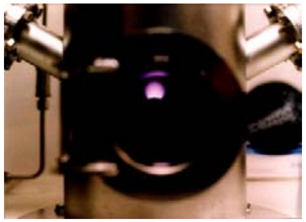

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[Yan *et al*. *Phys. Stat. Sol.* 201, R27 (2004)]

WHAT'S NEXT

Diamonds Find a Friend in the Semiconductor Sector

ANNE EISENBERG

…e who watches the Academy …ds knows, diamonds are still the …glamorous of gemstones. But as …echniques for synthesizing dia…ove, the stones may one day be …y on movie stars, but also in la…mitting diodes, integrated cir…her nondecorative but highly …lications.

…cause many diamonds can be …y in low-pressure chambers …n from a methane-hydrogen …axed into collecting and form…ystals around tiny starter dia… process yields large, rapidly …monds that may one day find a …g other things, semiconductor …h-temperature environments.

…y is growing diamonds," said …s, a professor of engineering at …n Reserve University who was …leveloping the technique of cre…ds from gases, called chemical …tion.

…egie Institution of Washington, … have now adapted the tech…e thick single crystals of dia…ot only grow extremely rapidly … out to be considerably harder …diamonds.

…quantify how hard the diamond … tends to damage the instruments used to measure it," said Russell J. Hemley, a senior staff scientist at Carnegie.

The research group, which began looking into the vapor deposition method four years ago, has created diamonds as thick as about one-fifth of an inch and as wide as two-fifths of an inch, Dr. Hemley said.

Dr. Hemley, a member of the institution's Geophysical Laboratory, said his interest in diamonds was related to basic research in the behavior of materials at extreme pressures. "We need large, perfect diamonds to make high-pressure devices for our research," he said. But diamonds like the ones the group has grown will have many other uses, including electronics, he said.

Apollo Diamond, a Boston company, is also growing large, single crystal diamonds by using a version of the chemical vapor deposition method, said Robert C. Linares, a founder of the company.

Researchers have long sought ways to use diamonds as a more durable alternative to silicon, which does not stand up as well to high temperatures and stress. But many early diamonds made by vapor deposition were poorly suited to electronic applications because they emerged in the form of a film with a jumble of diamond crystals oriented in varying ways, leading to defects that could trap electrons.

The researchers at Carnegie grew their diamonds from a gaseous mixture heated to high temperatures to produce the carbon that condensed on a diamond kernel. "We start with a seed, and the carbon atoms then rain out from the plasma, arranging themselves as a single crystal rather than as a film," Dr. Hemley said. Afterward the diamonds are heated to more than 3,600 degrees Fahrenheit and put under pressure to harden them further.

Physica Status Solidi

RESILIENT A synthetic single-crystal diamond created from gases in a technique known as chemical vapor deposition.

Semiconductor devices are one of several areas in which the new generation of synthetic diamonds may find use. Currently most transistors, diodes and integrated circuits are based on silicon, which is "doped" with impurities to alter the flow of electrons.

Diamond has a crystal structure similar to that of silicon and shares many of its properties.

But turning diamonds into semiconductors has proved a tough job, primarily because of the difficulties in doping diamonds, which are natural insulators, to improve their electrical properties. Doping diamonds with boron has worked well to turn them into a type of semiconductor called a p-type or p-diamond, for the positive charges that carry current.

But transistors and diodes also need a second kind of doped semiconductor material, called n-type, and that diamond has turned out to be hard to devise.

"The major outstanding problem for diamond semiconductor electronics is the lack of a good n-type doping agent," said James E. Butler, a research chemist at the Naval Research Laboratory who has conducted diamond research for 17 years, primarily working on improving the chemical vapor deposition process. "Without it, diamond electronics will be seriously limited."

N-type diamonds have been developed, including some that use phosphorus, he said, but none of the materials are entirely satisfactory. Last year Dr. Butler and colleagues reported that they had created a boron-doped diamond grown by vapor deposition that was then treated with deuterium.

"It's an n-type and it's reproducible," Dr. Butler said. "But we don't yet understand the fundamentals."

At Case Western, Dr. Angus and his colleagues have been making progress, although their solution is far from perfect, he said. Working with a doctoral student, Sally Eaton-Magana, now a postdoctoral associate at the Naval Research Laboratory, he doped vapor-produced diamonds with both boron and sulfur. "We added two elements at the same time to achieve n-type behavior," he said. It works, he added, but … trons don't move fast enough.

Dr. Angus says the problem migh… the doping seems to work only in t… surface region rather than un… throughout the diamond, a necessity … trollable properties. "You don't w… electrical properties to vary wi… throughout the semiconductor," he s…

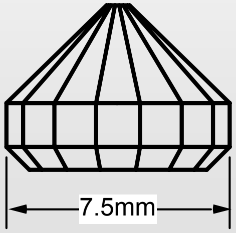
Dr. Butler said that synthetic di… might find their niche not in microp…ors but in high-current high-voltage …tions — for instance, in switching … for high-speed trains. These trains … 10,000 volts or so, he said, and use s…ductors to help control the power. C… the cars use big semiconductor waf… related heavy gear that add up to ro… ton per railcar.

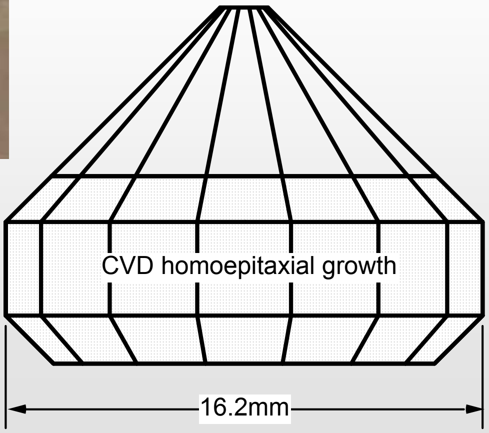
"But in the future diamond could … to take that ton of electronics and … down to a hundred pounds," he said.

Despite the problems that remai… solved, many researchers are hope… the new generation of synthetic di… will play a role in computers. "Chips …ting hotter and hotter, the more tra… you add," said Jimmy L. Davidson, a …sor of electrical and computer engi… at Vanderbilt University who ha… worked in diamond research. Silico… working at about 200 degrees Fahren… said, but diamond has internal pr… that allow it to work at 1,000 degree…enheit.

"When we put diamonds in compu… draw off heat," he said, "no fans will …ed."

…berg@nytimes.com





0.025 ct

0.25 ct

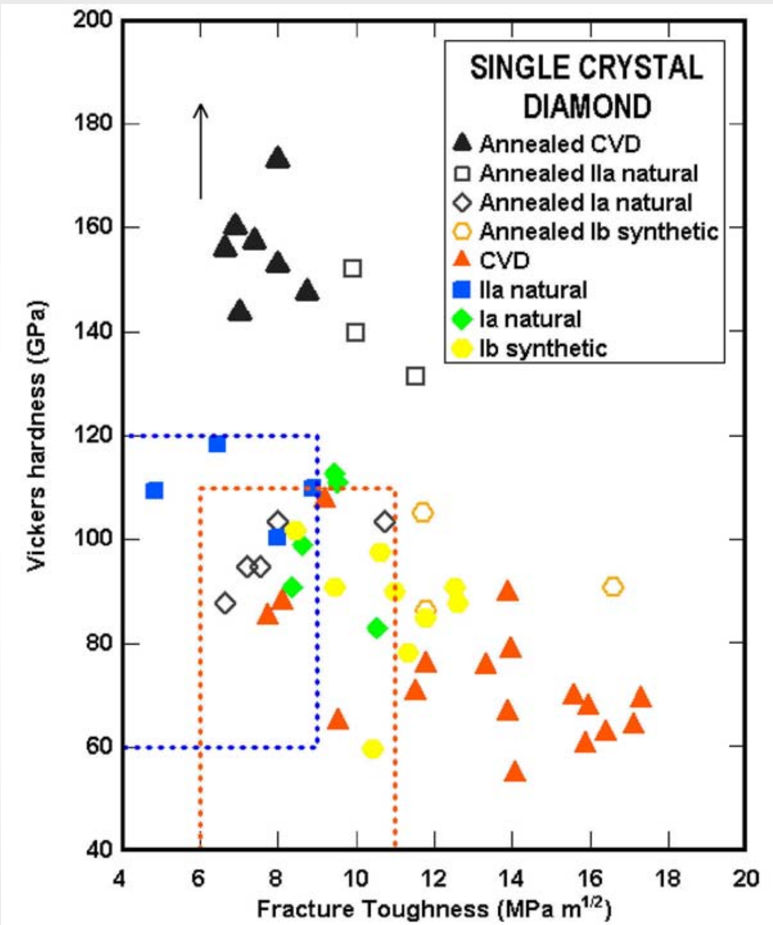
2.5 ct

25 ct

Carnegie Institution

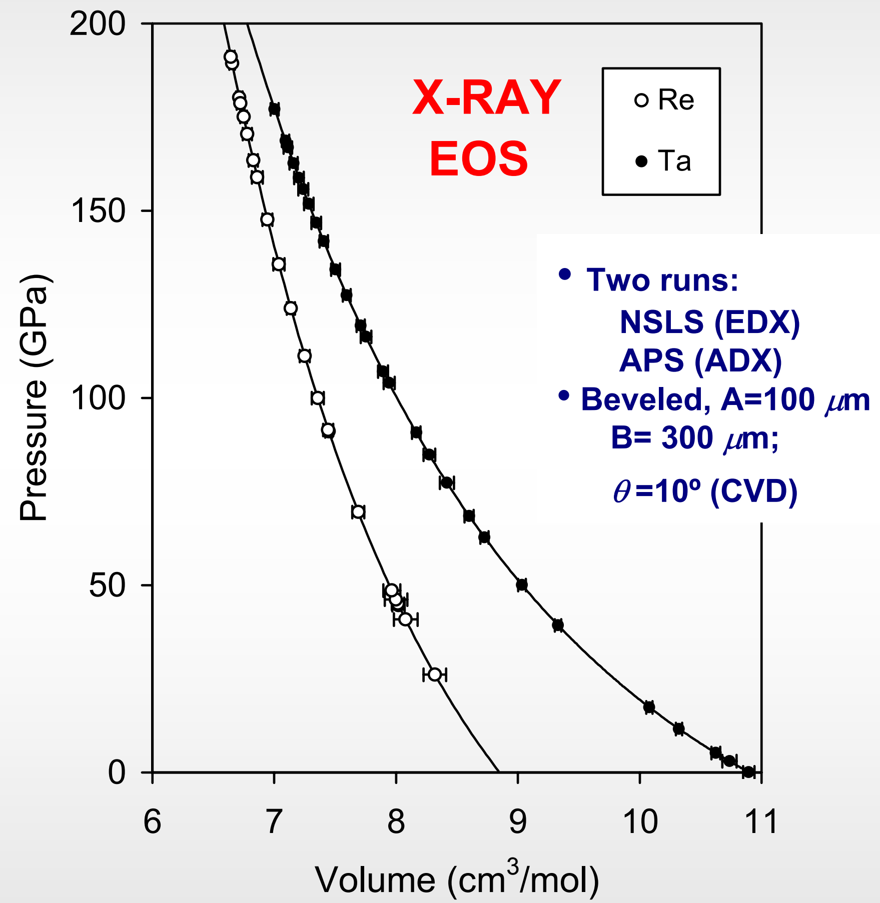
OPPORTUNITIES AND CHALLENGES:

Towards TPa Pressures with Large Volume Anvil Cells



CVD single crystals are utratough and/or ultrahard

[Yan *et al. Phys. Stat. Sol.* 201, R27(2004)]



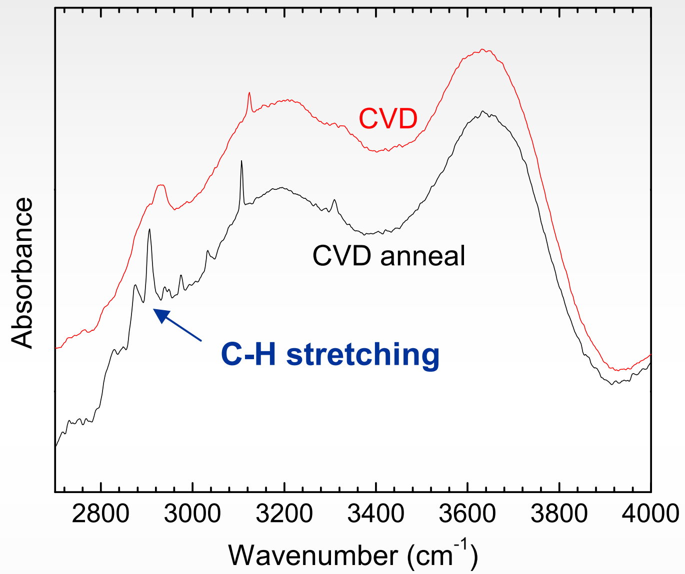
Single-crystal CVD anvils can generate multimegabar pressures

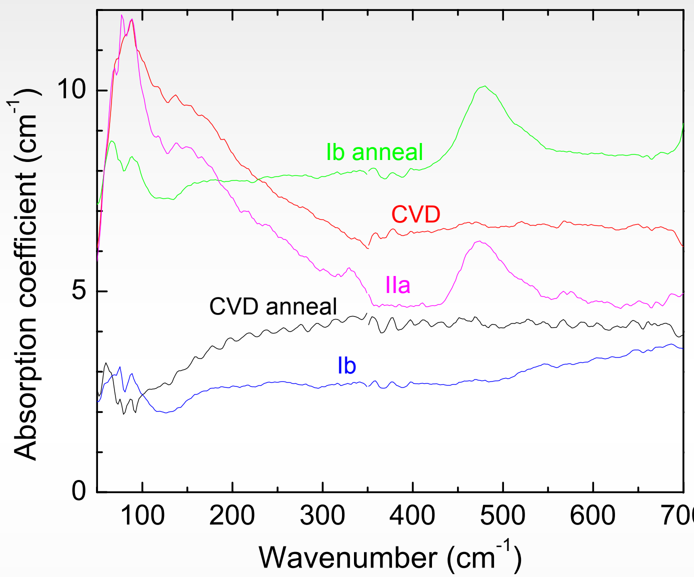
[W. Mao *et al., Appl. Phys. Lett.* 83, 5190 (2003)]

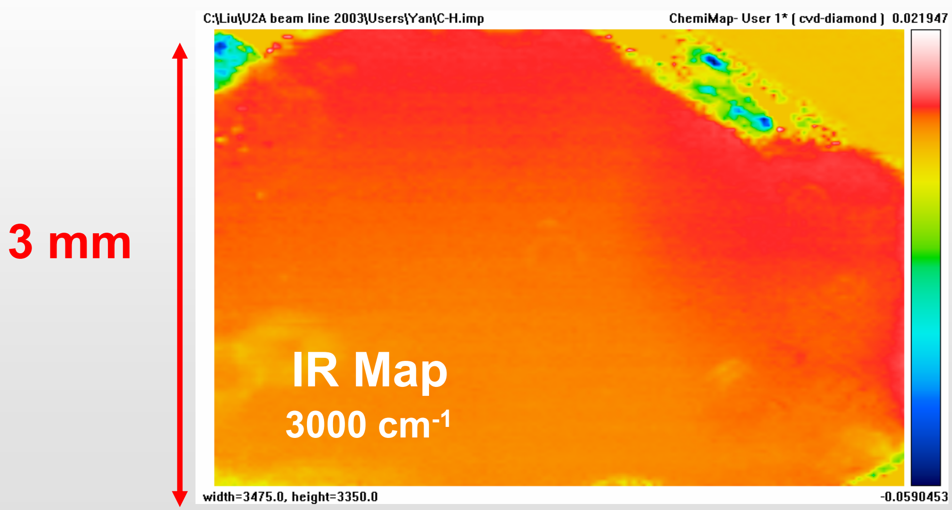
OPPORTUNITIES AND CHALLENGES:

Towards TPa Pressures with Large Volume Anvil Cells

Characterization of CVD diamond single crystals by synchrotron IR







- Unusual hydrogen impurity structure
- Largely homogeneous based on IR mapping
- Enhanced far-IR transparency on annealling
- X-ray topography (X19) in progress

CONCLUSIONS

1. High pressure: a superb application of synchrotron IR techniques, complementing hard x-rays and other methods.
2. An essential tool for uncovering new physics and chemistry of materials under extreme conditions.
3. Numerous problems in Earth and planetary science can now be addressed.
4. Particularly important are the new far-IR developments and integrated multi-probe approaches.
5. Numerous new high-pressure technique developments are coming on line to complement the new generation of synchrotron facilities: NSLS-II
6. The pressure parameter should be an integral part of sample environments at beamlines throughout NSLS-II.